

NASA CR 54535

PROTECTIVE COATINGS FOR CHROMIUM ALLOYS

by

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-7266

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 4.00

Microfiche (MF) 1.00

ff 853 July 85

N66 38147

(ACCESSION NUMBER)

122

(PAGES)

NR-54535

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

SOLAR, A DIVISION OF INTERNATIONAL HARVESTER

2200 PACIFIC HIGHWAY

SAN DIEGO, CALIFORNIA 92112

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## FOREWORD

This is the final summary report on a program initiated under National Aeronautics and Space Administration Contract No. NAS3-7266 and was administered by the Lewis Research Center, Cleveland, Ohio. The NASA project managers during the program have been Messrs. John Merutka and Robert Oldrieve, and the NASA Research Adviser was Salvatore Grisaffe. The report covers all work performed between 31 May 1965 and 30 June 1966.

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The Solar reference number for this program is S.O. 6-1871-7 and the internal report number is RDR-1398-2.

NASA CR 54535  
SOLAR RDR 1398-2

SUMMARY REPORT  
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prepared for

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20 AUGUST 1966

CONTRACT NAS 3-7266

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## ABSTRACT

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Three systems were investigated for the protection of the chromium-5 tungsten alloy:

- A simple silicide coating
- A nitrogen barrier coating, Re-(Ti, Cr, V)-Si
- An interstitial sink coating for control of nitrogen ingress to the substrate, V-(Ti, Mo)-Si

Both aqueous deposition and chemical vapor deposition techniques were studied for deposition of rhenium, but neither technique could be developed within the scope of the program to allow Re-(Ti, Cr, V)-Si to be evaluated as a coating. With the V-(Ti, Mo)-Si system, extensive process studies were undertaken to develop a practical coating process for vanadium. Electrolytic and nonelectrolytic fused salt techniques, and high- and low-pressure pack techniques were used to deposit this element. All processes could deposit vanadium, but the low pressure process using vanadium retorts produced the most uniform deposits.

Oxidation test on the V-Si, V-Mo-Si, V-Ti-Si, and V-Ti-Mo-Si system showed that by having unalloyed vanadium and/or molybdenum underneath the silicide layers, catastrophic oxidation of the substrate (not encountered on the uncoated alloy) can occur at 2400 F. The systems thus do not hold promise as reliable coatings for turbine blade applications. The simple silicide coatings, however, provided complete protection for the Cr-5W alloy for up to 500 hours at 2100 F permitting no oxygen or nitrogen ingress to the substrate.

Technical data were also developed on the V-Cr-Ti ternary system, the equilibrium partition of oxygen and nitrogen between vanadium and vanadium-titanium, and Cr-5W alloy. Similar empirical data were generated between silicon, nitrogen, and oxygen in the chromium alloy. Silicon, as the silicide, appeared to be both a barrier and an effective sink for oxygen and nitrogen.

*Author*

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# 1

## INTRODUCTION

The advantages of decreased engine weight and increased fuel efficiency, accruing from increasing the gas turbine inlet temperature, present a strong motivating force for the development of higher temperature turbine materials. The cermets, the refractory metals (tantalum and columbium primarily), and the fiber-reinforced metals have been or are being considered for possible application to blading in gas turbines for use at temperatures above 2000 F. The cermets have limitations resulting from brittleness and poor thermal fatigue resistance; the refractory metals must be coated to prevent catastrophic oxidation and thus depend on a thin, usually impact-sensitive coating for even limited life; the fiber-reinforced systems represent potential only at this stage of development since major fabrication problems and system optimization are required before these materials will be available for even limited testing. Of other systems that have received little attention, chromium alloys appear the most promising.

The properties of chromium, e.g., low density ( $7.1 \text{ gm/cm}^3$ ), high melting point, freedom from allotropic transformations, good oxidation resistance, excellent availability and, with alloying, high strength at 2000 F and above, indicate that it is a definite candidate material system. The superior oxidation resistance of chromium, as compared to the refractory metals, provides the alloy with a margin of safety if damaged in high-temperature service that cannot be equaled by the coated refractory metals. Chromium does have its weaknesses, however, which are severe embrittlement by nitrogen and high vapor pressure. Chromium requires protective coatings to:

- Control the ingress of nitrogen to the alloy
- Decrease the activity of chromium and thus lower its vapor pressure
- Increase the oxidation resistance in the temperature range of 1800 to 2400 F

Two coating-system approaches were initially scheduled for investigation to improve the surface stability of Cr-5W alloy operating to 2400 F. The short range

goal was a coating that would provide protection for 600 hours and the long range goal a coating that would provide protection for 3000 hours.

The two coating systems proposed for study were:

1. A metallic diffusion barrier type

Cr Alloy	Cr Re Alloy	(Cr, Ti)Si <sub>2</sub> , (Ti, Cr, V)Si <sub>2</sub>
-------------	-------------------	--

2. A nitrogen sink type

Cr Alloy	Cr V Alloy	(Cr, V)Si <sub>2</sub> , (Cr, Ti, Mo)Si <sub>2</sub>
-------------	------------------	--

Coating system Number 1 was characterized by an all-metal nitrogen barrier, rhenium. Chromium and titanium were added to the system to improve the low temperature oxidation resistance of the disilicide (ReSi<sub>2</sub>), and vanadium was added to control expansion and increase the refractoriness of the silicide. The silicide and SiO<sub>2</sub> would act as the primary nitrogen barriers.

Coating system Number 2 consisted of a sink to hold nitrogen in solution in a ductile form. Modification of this system to improve its performance included the addition of titanium with the vanadium to improve the capability of the sink, and additions of molybdenum to raise the melting point and reduce expansivity of the disilicide.

As control systems, both uncoated and straight silicide coated Cr-5W alloy specimens were carried through the test program.

# 2

## SUMMARY

The objective of this research program was the development of oxidation resistant coatings for use at 2400 F in air on chromium-base alloys. Two concepts were used as guidelines for the program. Concept No. 1, Re-(Ti, Cr, V)-Si, required the use of rhenium as a secondary nitrogen barrier, overlaid with metals which would form more oxidation resistant disilicides. The second concept, V-(Ti, Mo)-Si used interstitial sinks to control nitrogen ingress through silicide coatings. This report summarizes both basic data supporting the concepts, the performance of the coating systems, and the future potential developments of these systems. In addition to the primary systems, uncoated and the simple disilicide coated Cr-5W alloy were carried through the test phases of the program.

At the program outset, it was believed that sigma-phase formation between the rhenium nitrogen barrier and the chromium alloy would produce a brittle layer and that long time diffusion would be required to reduce the rhenium content below 67 weight-percent. Experimental studies, however, showed that rhenium, diffusion bonded to Cr-5W alloy, did not produce a measurably thick, brittle, sigma-phase layer after exposure for as long as 30 hours at 2400 F; thus this concept appears to be practical from a technical point of view. However, it was shown in subsequent studies that the state-of-the-art of rhenium deposition onto chromium, either by aqueous plating or by chemical vapor deposition, was not sufficiently developed to warrant the inclusion of the original concept in this program. The program was not set up to develop techniques for the deposition of this element. Research activities on the metallic nitrogen barrier concept, Re-(Ti, Cr, V)-Si, were terminated before any oxidation tests were actually performed.

The second system, V-(Ti, Mo)-Si, was designed to control the ingress of nitrogen to the substrate by interstitial sinks. This portion of the program included experimental work which provided confirmation of basic property data including the effectiveness of vanadium and titanium as sinks for nitrogen and the effectiveness of

vanadium as a material to destabilize the brittle titanium-chromium Laves phase ( $\text{TiCr}_2$ ). In the Laves phase destabilization work, it was shown that a ternary alloy of Cr-Ti-V containing as little as 30 percent vanadium, with chromium and titanium contents in the same ratio as in the  $\text{TiCr}_2$  Laves phase, is essentially all beta solid solution with a relatively high degree of ductility.

The effectiveness of vanadium and combinations of vanadium and titanium as interstitial sinks for nitrogen was also determined by diffusion bonding foils of these elements to the surface of Cr-5W alloy. The specimens were subsequently exposed to a pure, dry, nitrogen environment for up to 96 hours at 2400 F. The results showed that both elements can maintain an equilibrium concentration of nitrogen in the chromium alloy of less than 140 ppm. The vanadium-titanium combination was particularly effective and could maintain a nitrogen level for 96 hours of under 19 ppm. It appears that a technique utilizing either vanadium or vanadium-titanium is a practical means of reducing interstitial levels in the chromium in the "as-fabricated" condition. For example, in just one hour exposure at 2400 F, a surface layer of either vanadium or vanadium-titanium will reduce the nitrogen content in Cr-5W to below 3 ppm from the initial as-received value of at least 76 ppm.

In process studies, the two major development areas were in the application of rhenium and the application of vanadium. At the outset of the program, it was anticipated that rhenium could be readily deposited on chromium by the chemical vapor deposition technique from the chloride system. However, it turned out that consistent depositions by this technique were not attainable within the time allotted to this portion of the program. The deposits were nonuniform and, in many cases, the substrate was severely corroded. The fluoride system appeared to afford more potential because of lower temperature of deposition, and a few isolated specimens were coated uniformly, but within the scope of this investigation it was not possible to develop a technique which could uniformly deposit the rhenium-nitrogen barrier. A minor investigation was also carried out on the deposition of rhenium from aqueous solution using the potassium or ammonium perrhenate systems. However, in both cases, a discontinuous deposit was developed. Rhenium does not apparently deposit from the aqueous system in a coherent metallic form. When the deposit is annealed, severe shrinkage occurs producing major cracking of the coating and separation from the substrate.

In an effort to develop uniform coatings of vanadium on Cr-5W, four different techniques were used to deposit this element. These were electrolytic and nonelectrolytic fused salt deposition, and high-pressure and low-pressure pack deposition. Both fused salt techniques could be used to deposit vanadium, but deposits tended to be non-uniform, nodular, and the fused salt baths tended to be very sensitive to temperature gradients. Massive amounts of vanadium could form on the surface of the bath as an apparent result of the driving potential resulting from the difference in temperature between the anode and the surface. Of the two pack processes studied, the low-pressure process provided the softest vanadium deposit. With this process, a number of variables were studied, such as temperature, activator, and retort materials. The process was extremely sensitive to temperature. At temperatures above 2200 F, severe selective corrosion or vaporization of the chromium substrate was encountered. Of the activators studied, a mixture of sodium fluoride and potassium-vanadium fluoride ( $K_2VF_5$ ) appeared to give the smoothest deposit although the other activators gave equivalent deposition rates.

The vanadium pack deposition process appeared to be extremely sensitive to the retort material and perhaps to retort size. The most uniform vanadium deposits were obtained in vanadium retorts, which eliminated all secondary electrochemical effects except those derived from differential temperature. With vanadium retorts, no dendritic deposits were formed but some sintering of the pack to the specimens did occur. However, with tantalum retorts, deposits were obtained which were directional and dendritic. The dendrites formed on the side facing the retort. Also, the deposits obtained with tantalum retorts contained tantalum in addition to vanadium and were high in hardness, apparently as a result of solid solution hardening or Laves phase ( $TaV_2$ ) formation. The optimized vanadium deposition process was a sodium-potassium-vanadium fluoride activated vanadium pack in a vanadium retort. With this combination, up to 15 mg per square centimeter ( $15 \text{ mg/cm}^2$ ) of vanadium could be deposited at 2150 F in 15 hours.

No problems were encountered in the deposition of titanium and silicon. The titanium was deposited from a 2000 F nonelectrolytic fused fluoride salt bath that had been developed on an Air Force Contract (AF33(615)-3173). Silicon was deposited in a standard 1800 to 2150 F high-pressure pack. In the systems requiring molybdenum, this element was deposited by chemical vapor deposition at 1800 F from the chloride vapor phase.



Cyclic oxidation tests on the V-Ti-Si, V-Mo-Si, V-Ti-Mo-Si and V-Si applied to Cr-5W showed one particular weakness in the coating system that would probably preclude the application of this type of system to the protection of chromium alloys. This weakness is the catastrophic failure of the substrate upon the breakdown of the coating. The presence of  $\text{MoO}_3$  or  $\text{V}_2\text{O}_5$  appears to be responsible for this accelerated rate of attack. Of all of the systems exposed to oxidation testing, only simple silicided Cr-5W alloy showed merit as a coating system. The simple silicide provided protection for 500 hours at 2100 F. After a 500-hour exposure at 2100 F, the silicided specimens showed (in the Cr-5W substrate) a nitrogen content of 67 ppm and an oxygen content of 8 to 100 ppm, whereas the uncoated alloy showed values of 6700 ppm  $\text{N}_2$  and 4000 ppm  $\text{O}_2$ . Without modification, the simple silicide coating is inadequate to protect the Cr-5W alloy for more than 100 hours at 2400 F. However, in 120 hours, only a slight increase in the nitrogen content (to 120 ppm) was observed whereas nitrogen content in the uncoated material increased to 2.75 percent under comparable exposure. An initially thicker silicide layer might be expected to offer complete protection for an extended time. The experimental results discussed above indicate that silicon acts as both an oxygen barrier and as an interstitial sink material to control the ingress of oxygen and nitrogen to the substrate. The free energies of formation of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  are sufficiently negative to make it thermodynamically possible for silicon to not only control ingress of nitrogen and oxygen, but also to remove these interstitials from the substrate. Vacuum fusion analyses indicated that these partition effects were occurring during the 1500 F oxidation tests.

# 3

## METALLURGICAL BASIS FOR THE CONCEPTS

### 3.1 INITIAL BASIS FOR THE CONCEPTS

At the initiation of the program, two coating concepts for the protection of chromium alloys were adopted. Coating No. 1 was a nitrogen barrier system, plus an oxidation resistant outer silicide coating, with rhenium as the metallic nitrogen diffusion barrier. Coating No. 2 incorporated a vanadium-rich alloy layer to act as a nitrogen sink or getter, with a modified silicide coating for the primary oxygen and nitrogen barrier. Five modifications for each basic coating type were proposed.

#### 3.1.1 The Rhenium Nitrogen Barrier Coating

Rhenium was a logical choice for the nitrogen barrier for a number of reasons. These reasons include:

- Ductilizing effect on chromium
- High melting point and slow diffusion rate
- Low solubility for nitrogen
- High solubility in chromium, titanium, and vanadium

In the absence of experimental data, it was assumed that long-term annealing treatments would be required for form a homogeneous  $\alpha$  solid solution containing less than 67 weight-percent rhenium; the  $\alpha$  solid solution/ $\alpha + \sigma$  phase boundary (Fig. 1). It was anticipated that the low heat of formation of rhenium nitride would be effective in controlling the solubility of nitrogen in chromium-rhenium alloys. Recent work by Klein (Ref. 1) however, has shown that the solubility of nitrogen in chromium and chromium-35 weight-percent rhenium is the same, although precipitation of damaging nitride occurs much more sluggishly in the latter case. Klein proposed that the precipitation kinetics were controlled by the relatively slow substitutional diffusion of chromium or rhenium rather than the interstitial diffusion of nitrogen which would be rate controlling in unalloyed chromium. This would mean that more nitrogen is retained in solution in a chromium-rhenium alloy, and the embrittling effect of nitrogen would be substantially reduced. The proposed modifications in this system are shown in Table I.

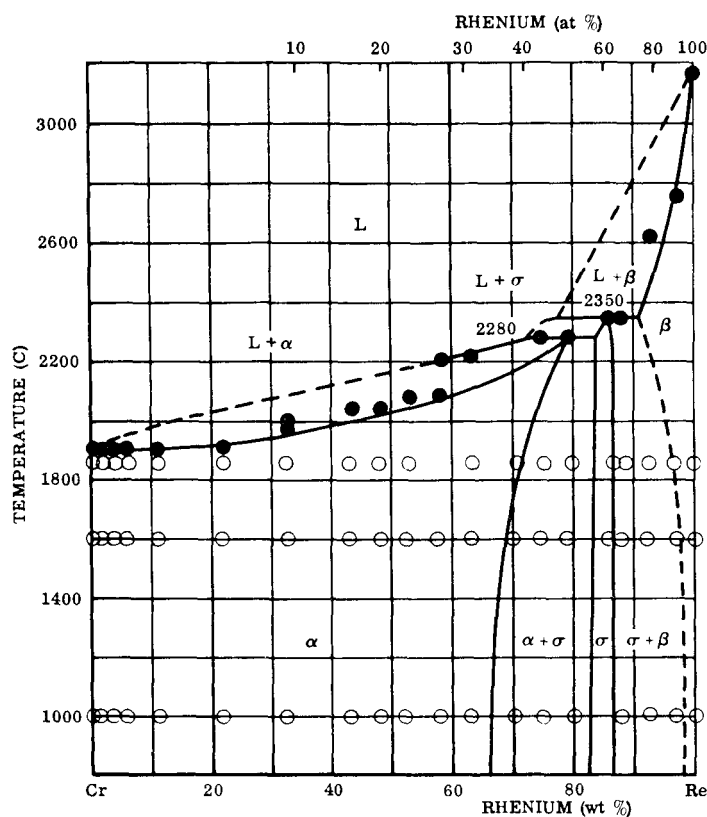


FIGURE 1. Cr-Re BINARY SYSTEMS

TABLE I

MODIFICATIONS FOR COATING SYSTEM NUMBER 1

Alloy	Modification (thickness in inches)				
	B1	B2	B3	B4	B5
Re	0.0005	0.0005	0.001	0.0005	0.0005
Ti-Cr	0.001	0.002	0.002	0.000	0.000
Ti-Cr-V	0.000	0.000	0.000	0.001	0.002
Si	0.002	0.002	0.002	0.002	0.002

Chromium and titanium additions were designed to improve the low temperature oxidation resistance of the disilicide  $\text{ReSi}_2$ , and vanadium was included because of its beneficial effect in lowering expansivity and increasing refractoriness (by promoting formation of an  $\text{SiO}_2$  glass) of the silicide.

### 3.1.2 The Nitrogen Sink Coating

This coating system was based upon the interstitial sink effect (predicted by theoretical work at Solar and later verified experimentally, Ref. 2). The sink effect is manifested by the uphill diffusion of interstitial elements that occurs when a metal that has a high solubility and forms very stable compounds with oxygen, nitrogen, and carbon, is heated in contact with a metal having a lower solubility and forming less stable compounds with these elements. Thus, titanium heated in contact with the carbide dispersion-strengthened columbium alloy, D43, will remove carbon from the columbium until equilibrium partition of carbon is attained (for this case about 100 to 16,800 ppm) resulting in a 40 percent strength loss in the columbium alloy.

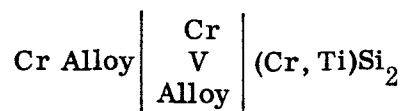
If the respective free energies of formation of two solid solutions are known, the equilibrium partition of interstitial element may be calculated. For the general case, the free energy of formation of a solid solution is given by

$$\Delta F_{M(I)} = \Delta F_{MI} + RT \ln \frac{X}{S}$$

where X is the concentration of interstitial element in metal M to form the solid solution M(I), MI is the compound in equilibrium with the saturated solution of I in M, and S is the saturation concentration of interstitial in metal M. The results of applying this approach to chromium, titanium, and nitrogen are shown in Figure 2. Figure 2 also shows that at 2100 F a saturated titanium/nitrogen solid solution will be in equilibrium with chromium containing  $2 \times 10^{-4}$  ppm nitrogen.

As a coating sublayer, the purpose of the sink was to retain in solution any nitrogen which might bleed through the primary silicide barrier, thus preserving ductility of the system. Since the brittle Laves phase is formed in the Ti-Cr system, it was proposed to use vanadium/titanium alloys. Based on the limited amount of thermodynamic data available, it was anticipated that pure vanadium by itself would act as an effective sink, while additions of titanium would serve to increase the efficiency of the sublayer.

The basic system was:



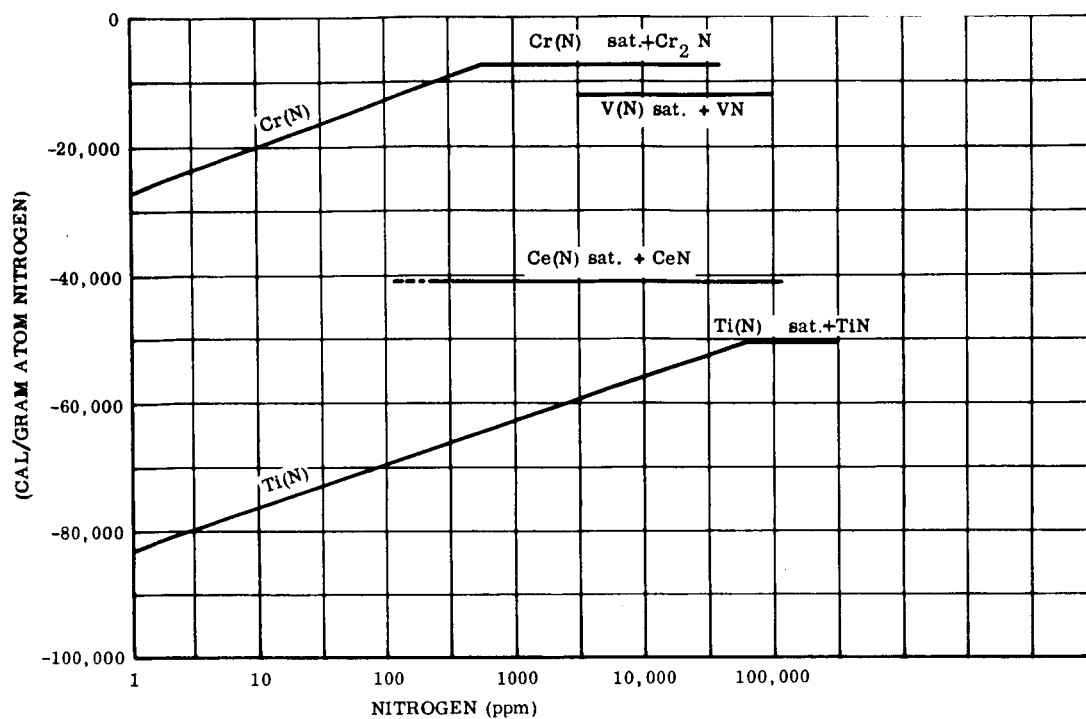


FIGURE 2. VARIATION OF FREE ENERGY OF FORMATION WITH NITROGEN CONTENT; Temperature 1420 K (2100 F)

and proposed modifications included titanium additions to improve the capability of the sink, and molybdenum additions to raise the melting point and reduce expansivity of the disilicide. Coatings C1 through C5, listed in Table II, were selected for study.

TABLE II

MODIFICATIONS FOR COATING SYSTEM NUMBER 2

Element	Modification (diffusion layer thickness in inches)				
	C1	C2	C3	C4	C5
Vanadium	0.002	0.002	0.002	0.002	0.002
Titanium	0.000	0.001	0.002	0.000	0.001
Molybdenum	0.000	0.000	0.000	0.001	0.001
Silicon	0.002	0.002	0.002	0.002	0.002

### 3.2 EXPERIMENTAL BASIS FOR THE COATING

Experiments were performed to study the feasibility or validity of certain aspects of the two coating systems. These experiments included diffusion studies on (Cr-5W)/Re diffusion bonded couples, Laves phase ( $\text{TiCr}_2$ ) destabilization by vanadium additions, and nitrogen diffusion studies to evaluate the effectiveness of vanadium and vanadium-titanium as a nitrogen sink when in contact with chromium.

Although these studies should be regarded as preliminary experiments, they were not necessarily performed chronologically, and some of this work was carried out concurrently with the coating process development.

#### 3.2.1 The Re-(Ti, Cr, V)-Si System - (Cr-5W)/Re Diffusion Studies

Diffusion couples were prepared by the yield stress controlled diffusion bonding technique in Solar's production bonding facility. Rhenium foil, 0.001 inch thick, was bonded on either side of Cr-5W sheet specimens (0.063 inch thick) using a pressure of 8000 psi at a temperature of 2400 F for 10 seconds. Using these conditions, a good diffusion bond was obtained. Specimens were then annealed at 2200 F for 15 and 30 hours and at 2400 F for 1, 15, and 30 hours under high-purity argon. The 30 hour samples were annealed in two cycles to observe the effects of thermal stresses (due to differences in thermal expansivity) on any brittle layers which might have formed. Specimens were prepared for metallographic observation and microhardness studies. The microhardness data are tabulated in Table III. The microstructures of specimens as-bonded, annealed at 2200 F for 15 hours, and annealed at 2400 F for 1 and 30 hours are shown in Figures 3 through 6.

TABLE III  
MICROHARDNESS DATA OF (Cr-5W)/Re

Condition		Microhardness - KHN Values (50 gm load)		
Temperature (F)	Time (hr)	Re Layer	Cr-5W/Re Interface	Cr-5W Matrix (center line)
As-bonded		683 to 735	426	259
2200	15	530	400	232
2200	30	390 to 800	312	245
2400	1	573	306	250
2400	15	713 to 735	581	245
2400	30	521 to 565	530	215

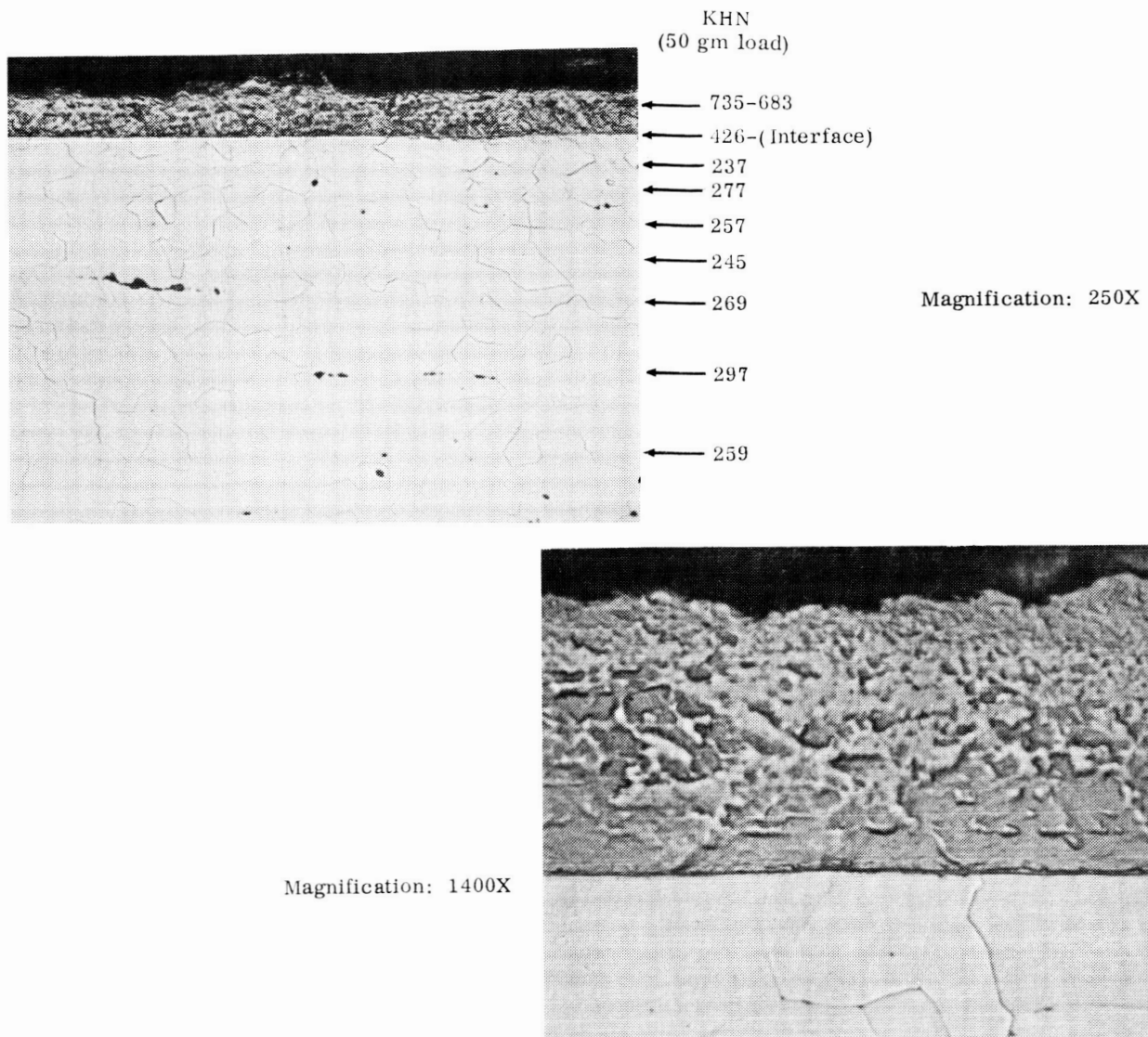
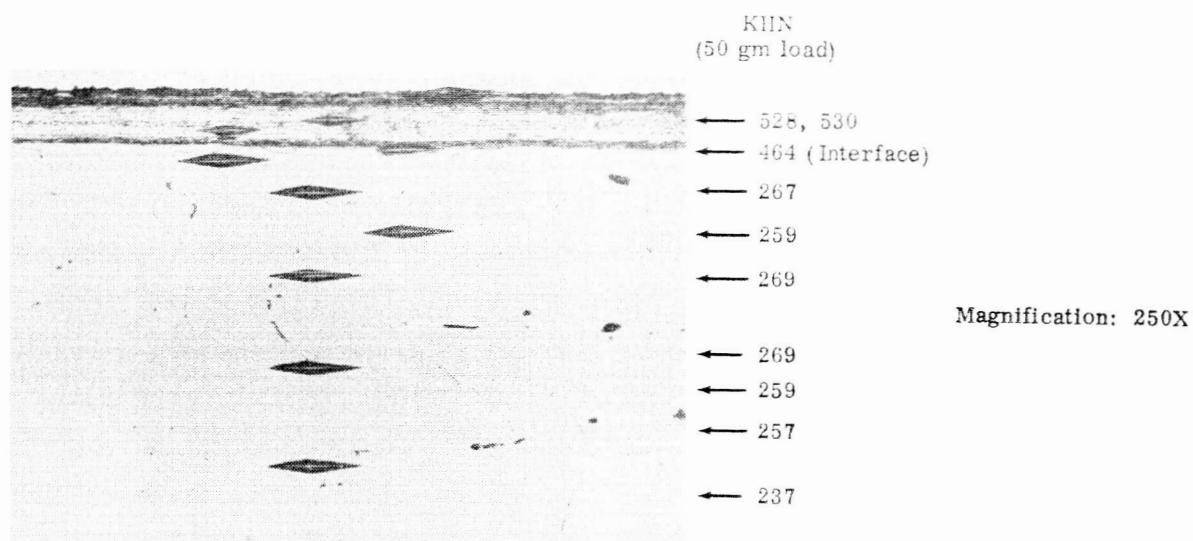


FIGURE 3. STUDY OF (Cr-5W)/Re DIFFUSION COUPLE; As-Bonded



Magnification: 1400X

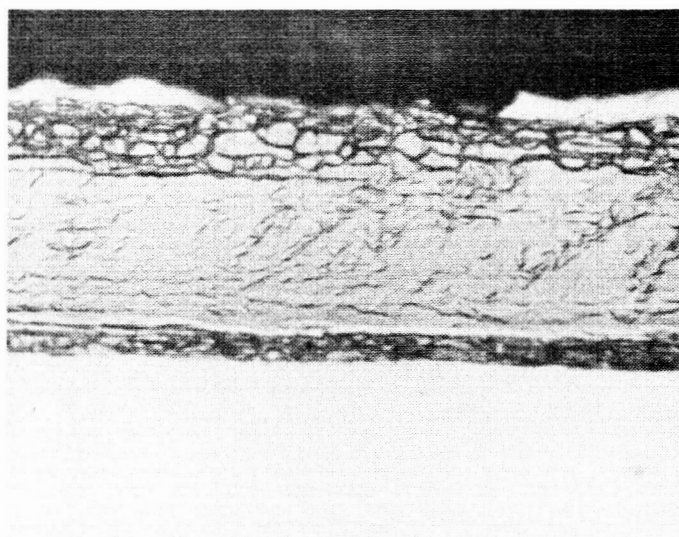


FIGURE 4. STUDY OF (Cr-5W)/Re DIFFUSION COUPLE; Annealed in Argon at 2200 F for 15 Hours



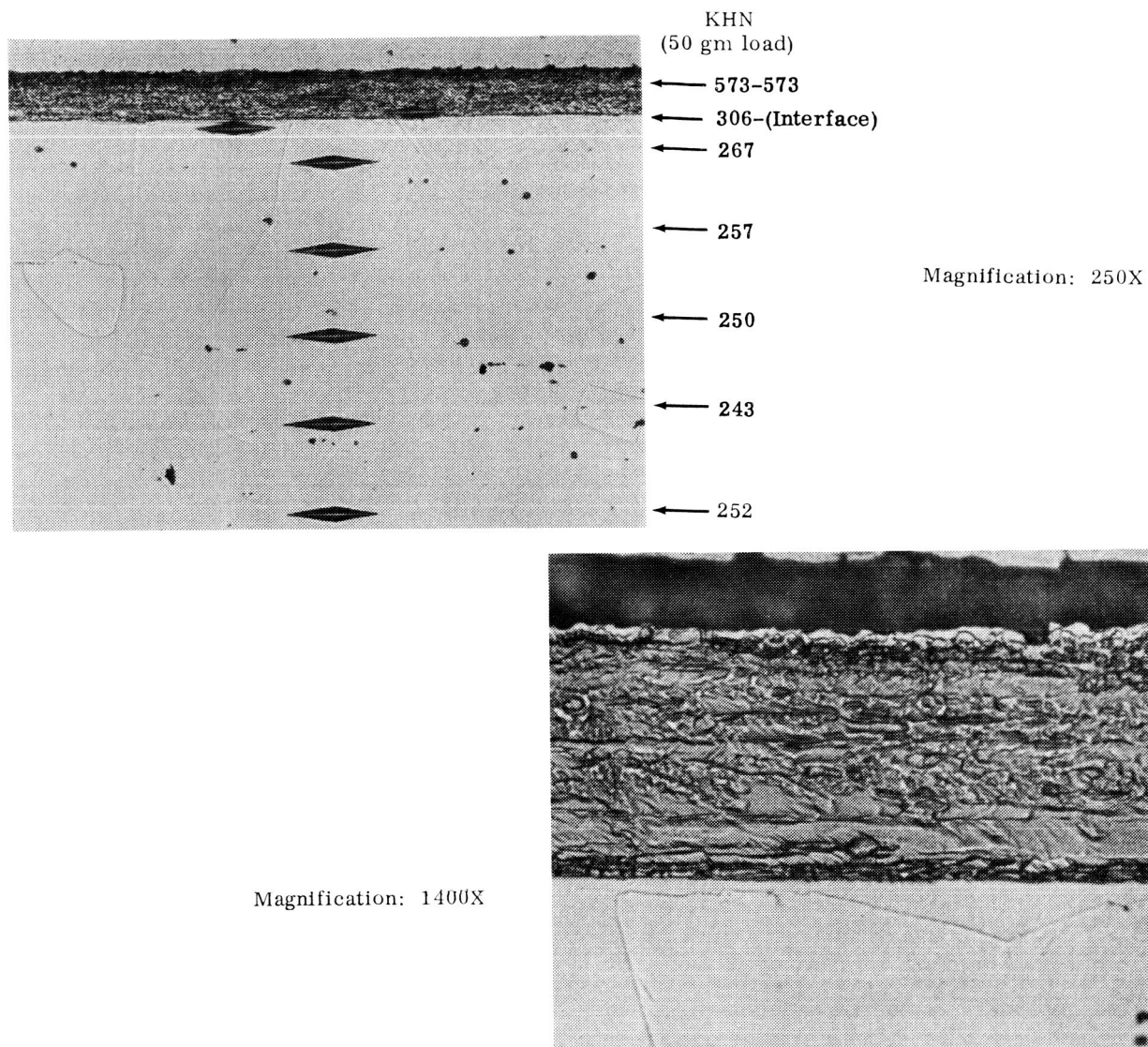


FIGURE 5. DIFFUSION STUDY OF (Cr-5W)/Re DIFFUSION COUPLE;  
Annealed in Argon at 2400 F for 1 Hour

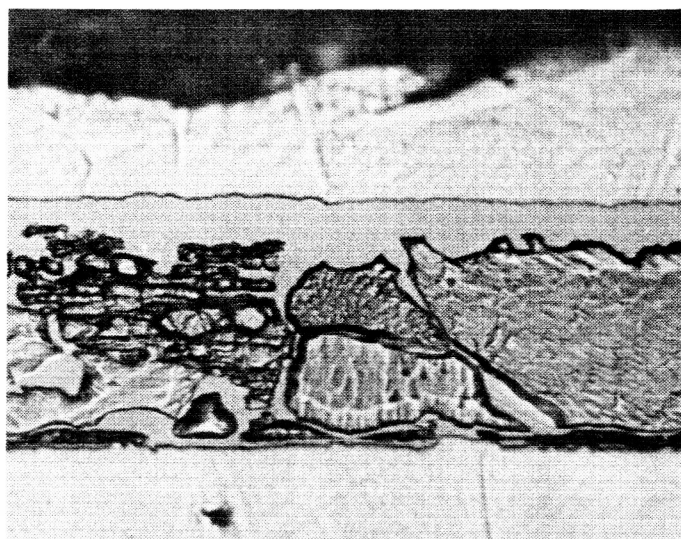
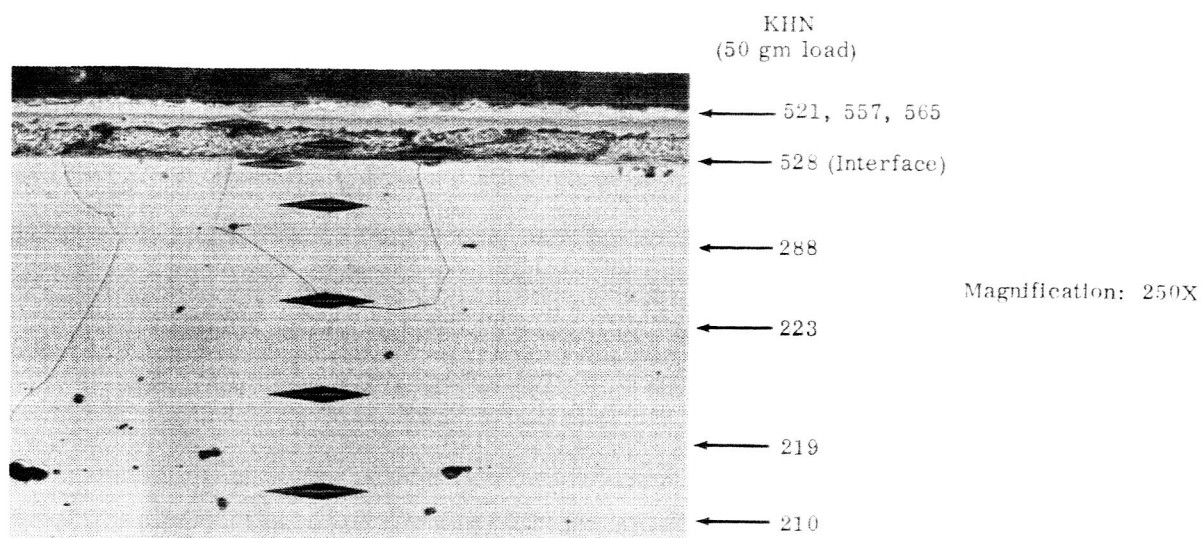


FIGURE 6. DIFFUSION STUDY OF (Cr-5W)/Re DIFFUSION COUPLE;  
Annealed in Argon at 2400 F for 30 Hours

During annealing the specimens were sandwiched between two pieces of Cr-5W alloy and then wrapped in tantalum foil to prevent contamination from residual  $O_2$  or  $N_2$ . Some vapor transfer of chromium occurred from the outer protective pieces of sheet onto the surface of the rhenium (particularly evident in Figure 5).

The as-bonded rhenium layer (Fig. 3) was essentially cold-worked metal. After the various annealing treatments, progressive recovery and recrystallization occurred in the rhenium. Of particular interest was the fact that little or no change in the thickness of this original rhenium layer occurred, even after 30 hours at 2400 F. That some solution of rhenium in the chromium occurred was evidenced by an increase in the interface hardness (extending to about 0.002 inch into the matrix after 30 hours at 2400 F), but no signs of a continuous  $\sigma$  phase was observed. Figure 5 is taken to represent a condition of about 30 percent recrystallization of the rhenium.

These data indicate that a pure rhenium layer in contact with the program alloy is stable (at least at 2400 F for up to 30 hours) and does not form an embrittling layer of  $\sigma$  phase. The hardness values also indicate that the rhenium layer will be relatively ductile.

The original concept of a rhenium alloy layer as a nitrogen barrier required diffusion of rhenium into the chromium substrate to form a homogeneous body-centered-cubic (bcc) alloy. This would place an upper limit for the rhenium content of 67 weight-percent, since formation of brittle  $\sigma$  phase occurs above this concentration. However, the work of Klein showed that the solubility of nitrogen in chromium is unchanged by the addition of rhenium up to a level of 35 atomic-percent (67 weight-percent) and therefore a Cr-35 atomic-percent Re alloy would not have an appreciable influence on the ingress of nitrogen and would not act as an effective diffusion barrier. Embrittlement due to nitrogen solution and nitride precipitation, however, would be greatly diminished in this alloy layer because of a pronounced change in precipitation kinetics and the tendency of rhenium to prevent grain boundary segregation.

Data obtained from the (Cr-5W)/Re diffusion couple studies show that the rhenium layer is surprisingly stable at 2400 F with:

- Interdiffusion occurring relatively slow
- No formation of a detectable  $\sigma$  phase layer after 30 hours at 2400 F (the maximum intended use temperature of the subject coating system)

Longer annealing studies are required to investigate the diffusional stability of the rhenium layer after hundreds of hours before the full potential of this particular nitrogen diffusion barrier system can be assessed. Difficulties encountered with application techniques for rhenium on chromium (discussed in a later section) led to the early abandonment of this system; however, recent vapor deposition experiments at San Fernando Laboratories (the original subcontractors for this work) have shown that there is some potential for this application technique.

### 3.2.2 The (V, Ti, Mo)-Si System

#### Destabilization of $\text{TiCr}_2$ Laves Phase

In the Ti-Cr binary system, a brittle Laves phase ( $\text{TiCr}_2$ ) is formed between 60 to 68 weight-percent chromium (Ref. 3). Vanadium and chromium form a continuous series of solid solutions, and vanadium/titanium alloys are also solid solution alloys, although a metastable  $\omega$  phase has been reported (Ref. 4) at 10 to 18 weight-percent vanadium, which is formed due to transformation of the titanium-rich, bcc solid solution. Formation of a continuous compound phase in a coating sublayer would be a serious problem in terms of poor ductility and the possibility of thermal-stress induced cracking causing the spalling away of large areas of coating.

A metallographic study was carried out to determine how much vanadium is required to suppress formation of the embrittling  $\text{TiCr}_2$  phase. Alloys containing 0, 2, 5, 10, 30, 50, and 80 weight-percent vanadium, with the balance of chromium and titanium in the ratio  $\text{TiCr}_2$ , were prepared by arc melting. The as-cast hardness values are shown in Figure 7 and the change in microstructure, going from the  $\text{TiCr}_2$  stoichiometric composition to an alloy containing 30 weight-percent vanadium is shown in Figures 8 through 11. Additional alloys containing 15 and 25 weight-percent vanadium were prepared and, with the 20 and 30 percent alloys, were solution treated (2400 F for 2 hours) and aged (2200 F for 12 hours). This treatment removed the coring and promoted grain growth. The resulting microstructures are shown in Figures 12 through 15.

At 15 weight-percent vanadium, continuous grain boundary  $\text{TiCr}_2$  phase was still evident (Fig. 12) in addition to spheroidized, discontinuous particles. Further additions of vanadium (20 to 30 weight percent) prevented formation of continuous grain

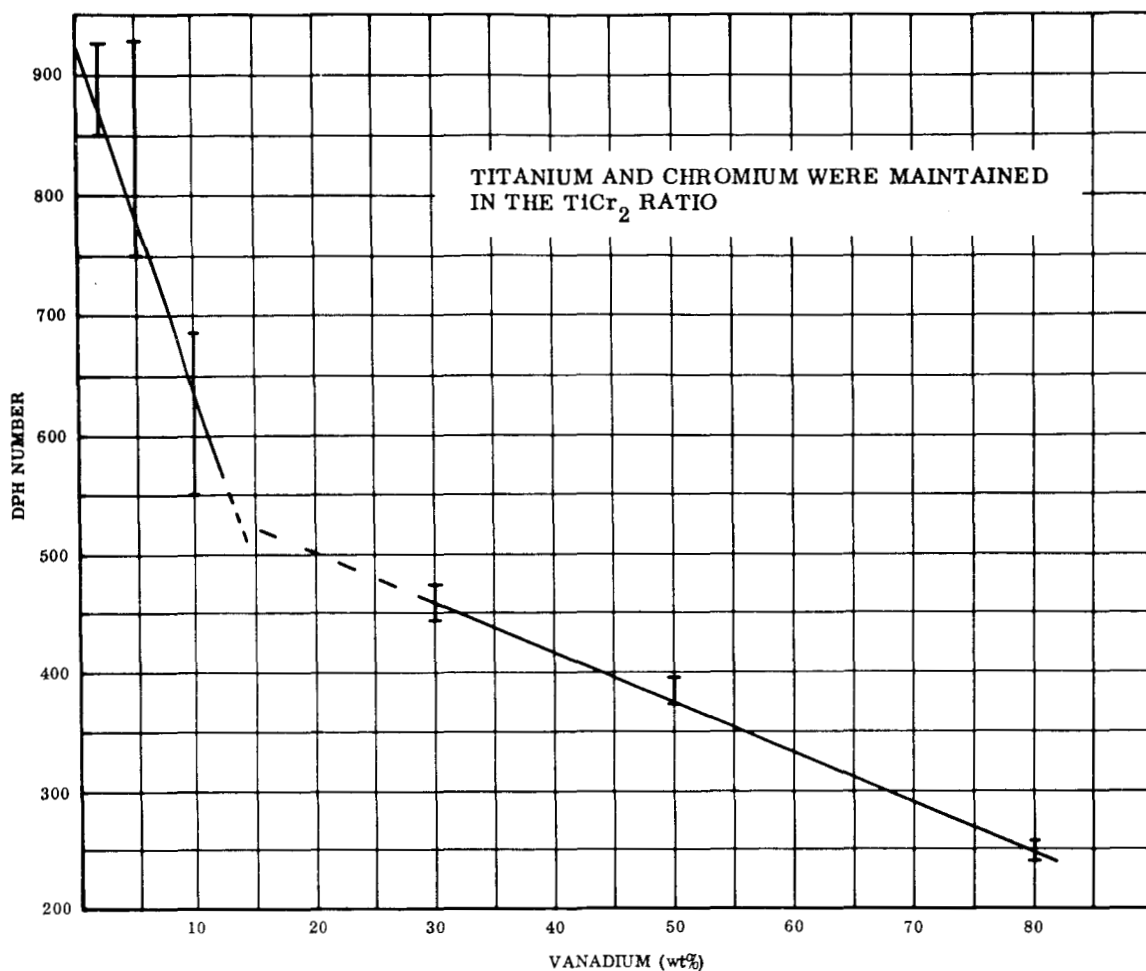
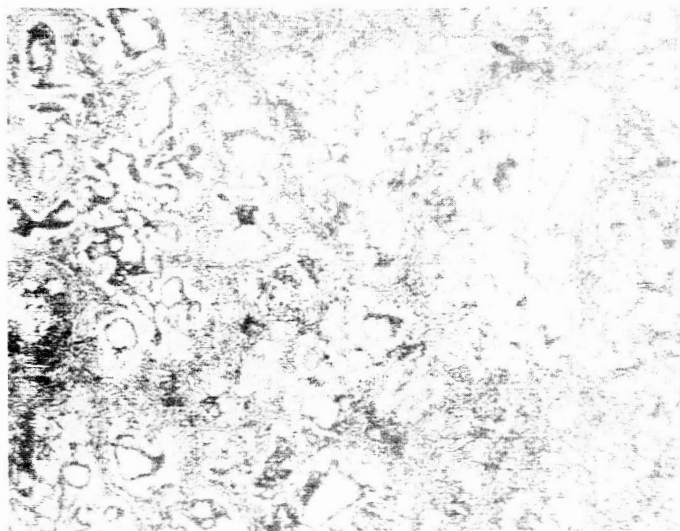


FIGURE 7. INFLUENCE OF VANADIUM CONTENT ON HARDNESS OF TITANIUM-CHROMIUM-VANADIUM ALLOYS

boundary networks of Laves phase. However, rounded precipitate particles were still evident, the morphology of which indicated that precipitation occurred on cooling from 2400 to 2200 F (Fig. 13 through 15) and subsequent holding at 2200 F caused the precipitates to agglomerate and spheroidize. Heavy etching revealed a very fine, intragranular Widmanstatten precipitation in all of the homogenized and aged alloys, which presumably occurred during fast cool down from 2200 F.

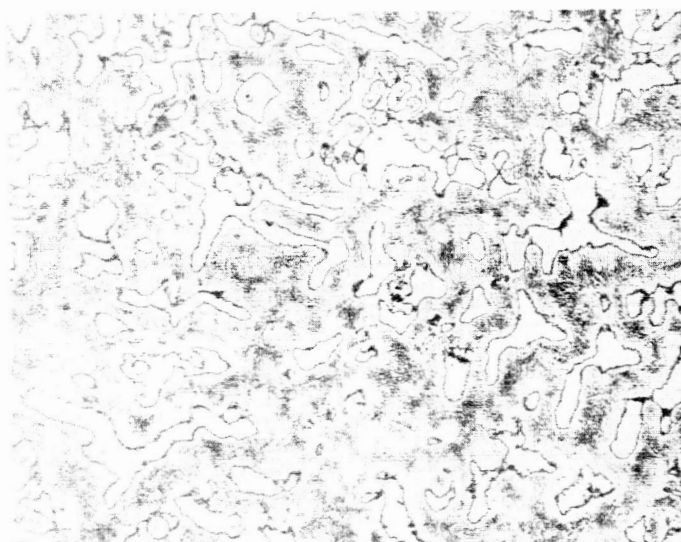
These hardness and metallographic data show that a ternary alloy of Cr-Ti-V containing as little as 30 weight-percent vanadium with the chromium and titanium content in the  $TiCr_2$  ratio, is largely a  $\beta$  solid solution, indicating a relatively high degree of ductility. Thus, providing a level of 30 weight-percent vanadium is preserved in the coating sublayer, embrittlement due to Laves phase formation will not become a serious problem.



Magnification: 250X

FIGURE 8.

ARC-MELTED ALLOY; 65.5 Wt%  
Chromium, 35.5 Wt% Titanium



Magnification: 250X

FIGURE 9.

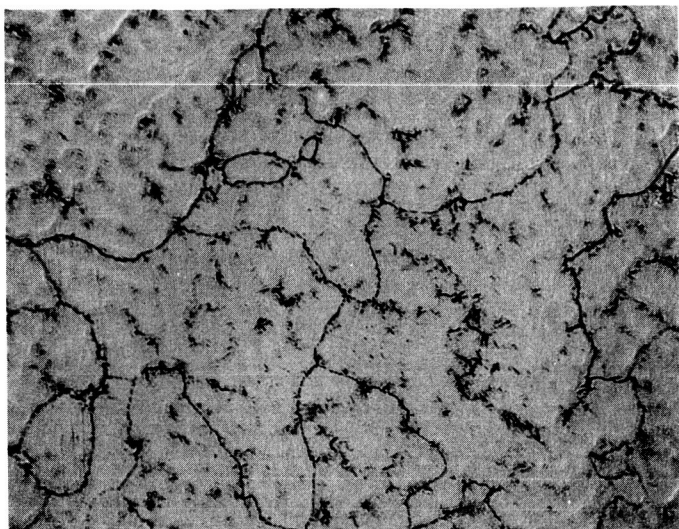
ARC-MELTED ALLOY; 61.0 Wt%  
Chromium, 34.0 Wt% Titanium,  
5.0 Wt% Vanadium



Magnification: 250X

FIGURE 10.

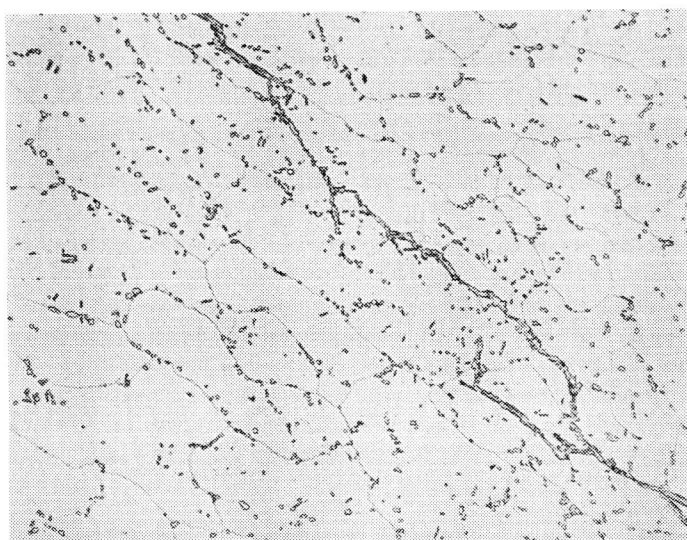
ARC-MELTED ALLOY; 58.0 Wt%  
Chromium, 32.0 Wt% Titanium,  
10.0 Wt% Vanadium



Magnification: 250X

FIGURE 11.

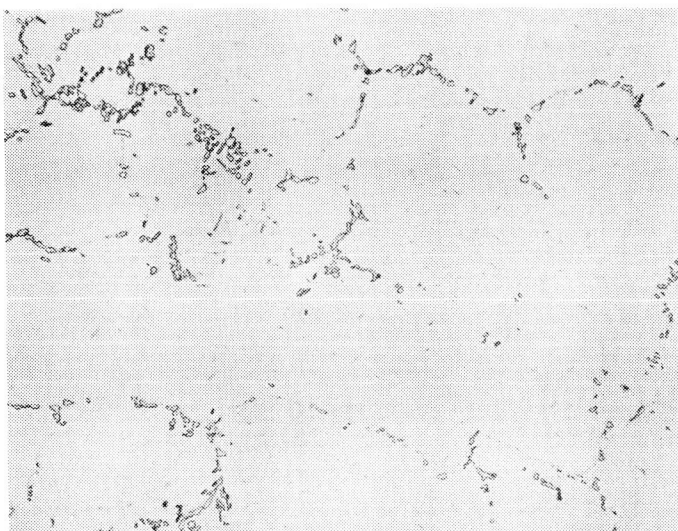
ARC-MELTED ALLOY; 45.0 Wt% Chromium, 25.0 Wt% Titanium, 30.0 Wt% Vanadium



Magnification: 250X

FIGURE 12.

ARC-MELTED ALLOY; 55.0 Wt% Chromium, 30.0 Wt% Titanium, 15.0 Wt% Vanadium. Homogenized and Aged in Argon



Magnification: 250X

FIGURE 13.

ARC-MELTED ALLOY; 51.5 Wt% Chromium, 28.5 Wt% Titanium, 20.0 Wt% Vanadium. Homogenized and Aged in Argon





Magnification: 250X

**FIGURE 14.**

**ARC-MELTED ALLOY; 48.0 Wt% Chromium, 27.0 Wt% Titanium, 25.0 Wt% Vanadium. Homogenized and Aged in Argon**

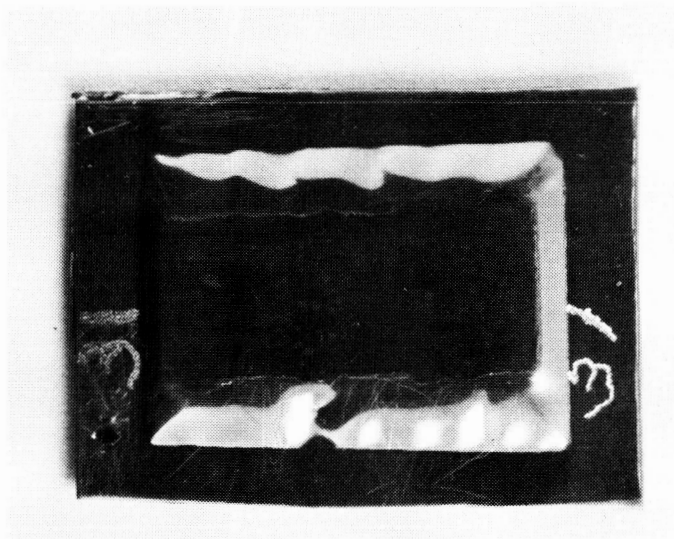


Magnification: 250X

**FIGURE 15.**

**ARC-MELTED ALLOY; 45.0 Wt% Chromium, 25.0 Wt% Titanium, 30.0 Wt% Vanadium. Homogenized and Aged in Argon**





Magnification: ~2X

FIGURE 16.  
DIFFUSION BONDED COMPOSITE

### Interstitial Sink Studies

A series of experiments were undertaken to establish the effectiveness of vanadium and vanadium-titanium layers on chromium as a sink or getter for nitrogen.

Coupon samples of Cr-5W alloy were sandwiched between pure metal foils, using the yield stress controlled diffusion bonding technique, so that intimate bonding was achieved over the specimen surfaces. The foils were then bonded together around the periphery of the samples to form sealed envelopes.

Typical bonding conditions were a pressure of 10 ksi applied for 20 seconds at 2400 F. A typical as-bonded specimen is shown in Figure 16. The following diffusion bonded composites were prepared by this technique:

- 0.060-inch (Cr-5W) - 0.010-inch V
- 0.060-inch (Cr-5W) - 0.010-inch V - 0.002-inch Ti
- 0.060-inch (Cr-5W) - 0.010-inch V - 0.002-inch Mo
- 0.060-inch (Cr-5W) - 0.010-inch V - 0.002-inch Ti - 0.002-inch Mo

Specimens were exposed to pure, gettered nitrogen at 2400 F for times ranging from 1 to 96 hours. They were then sectioned for metallographic examination and microhardness testing, and samples were taken for vacuum fusion analyses. The analyses for nitrogen were conducted predominately on the chromium alloy substrates with the outer metallic layers removed. In some instances, analyses were conducted on the vanadium or titanium layers to evaluate the partition of nitrogen between the substrate and coating.

The microstructures and microhardness values of the preceding diffusion bonded couples after various exposure times at 2400 F in pure nitrogen are shown in Figures 17 through 22 and 24. Vacuum fusion analyses data are summarized in Tables IV and V. The as-received Cr-5W alloy and the as-bonded (Cr-5W)-V and (Cr-5W)-V-Ti samples are shown in Figure 17. Temperature and time parameters of the bonding cycle were sufficient to allow the solid solution chromium alloy to recrystallize, with some drop in Knoop hardness values. A one-hour exposure of uncoated chromium at 2400 F to a pure nitrogen atmosphere resulted in formation of a uniform, 0.006 inch layer of compound (Fig. 18) with a KHN of 2300 to 2800 (50 gm load). Heavy grain boundary precipitates were formed in the underlying chromium, but no needles were apparent, indicating a more rapid grain boundary diffusion. (Rapid cooling would also reduce intragranular nitride precipitation.) All the samples exposed to nitrogen for one hour were given a further homogenization treatment of 2400 F for 24 hours in argon atmosphere. For the uncoated chromium alloy, this resulted in complete dissociation of the compound phase and caused the formation of columnar grains where compound had existed previously (Fig. 18B), again, an indication of rapid grain boundary diffusion of nitrogen. Vacuum fusion analysis (Table IV) showed low nitrogen content (0 to 76 ppm) and some oxygen contamination after the argon anneal. An exposure time of 24 hours in nitrogen was sufficient to convert all of the chromium alloy (0.060-inch thick) to compound (Fig. 18C) with no observable difference between this and the 96-hour sample.

TABLE IV  
VACUUM FUSION ANALYSIS FOR O<sub>2</sub> AND N<sub>2</sub> IN Cr-5W  
SUBSTRATE DIFFUSION COUPLE

Exposure Time (hr)	(Cr-W) Alloy		(Cr-W)-V		(Cr-W)-V-Ti		(Cr-W)-V-Mo		(Cr-W)-V-Ti-Mo	
	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)
0	0.085 to 0.225	0.0021 to 0.0023	0.01 to 0.1							
1.0 <sup>(1)</sup>	0.32 to 0.529	0 to 0.0076	0.0008 to 0.0009	Not detectable	0.0016	0.0003				
4	0 to 0.031	3.73								
24	0.085 to 0.107	5.95 to 7.78(2)								
96	0.101 to 0.130	4.98 to 6.40(2)	0.0055 to 0.0065	0.010 to 0.014	0.0058 to 0.0112	0.0019 to 0.0013	0.0033 to 0.0042	0.0051 to 0.0097	0.0019 to 0.0029	0.0002 to 0.0005
1. One-hour in N <sub>2</sub> + 24 hours in argon 2. Values are low, based on microstructure, X-ray diffraction, and micro-Kjeldahl analyses										

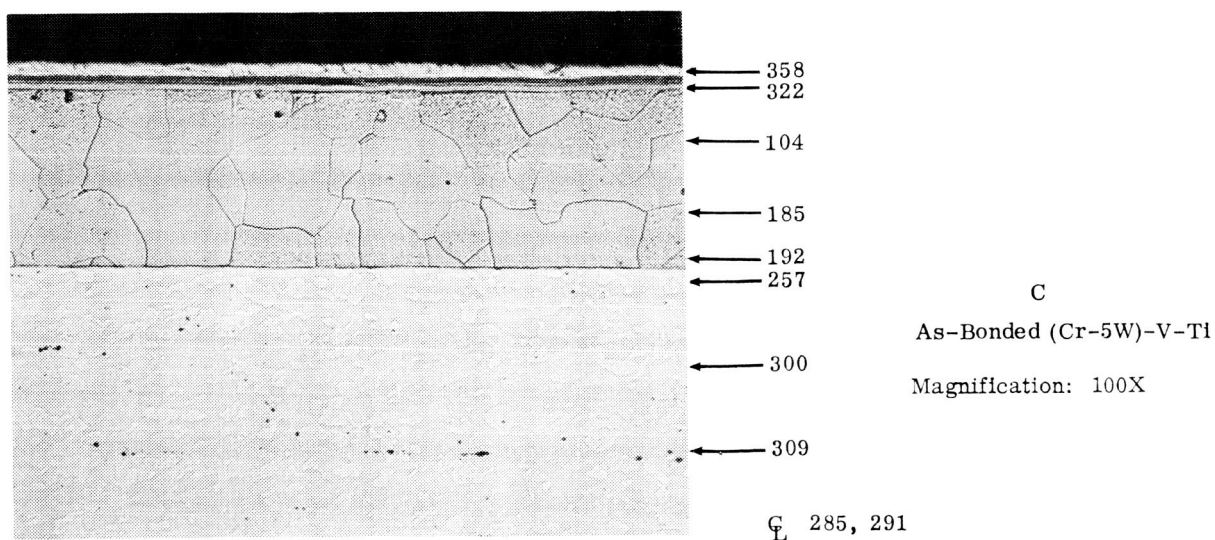
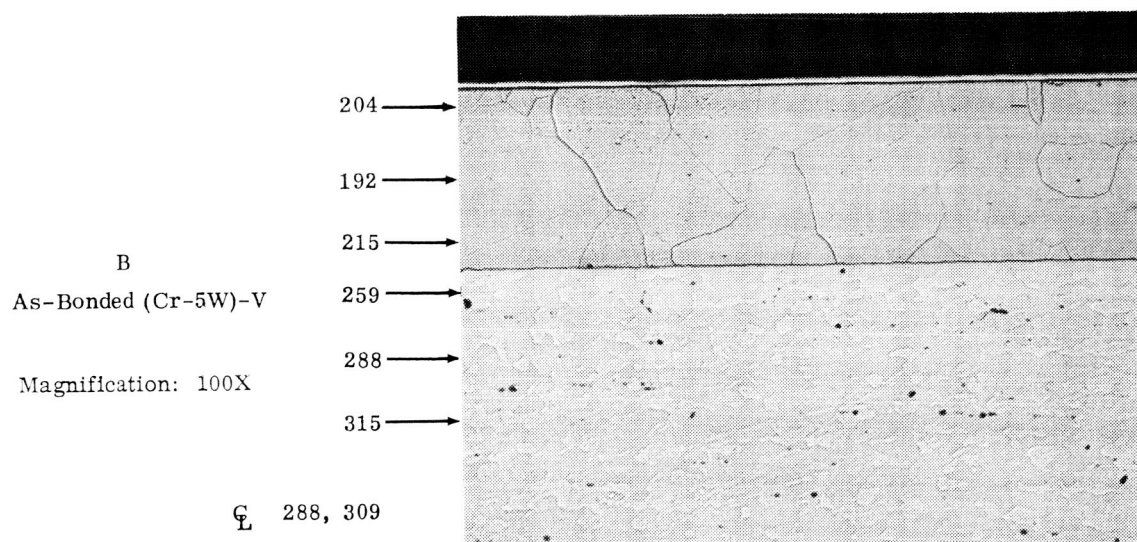
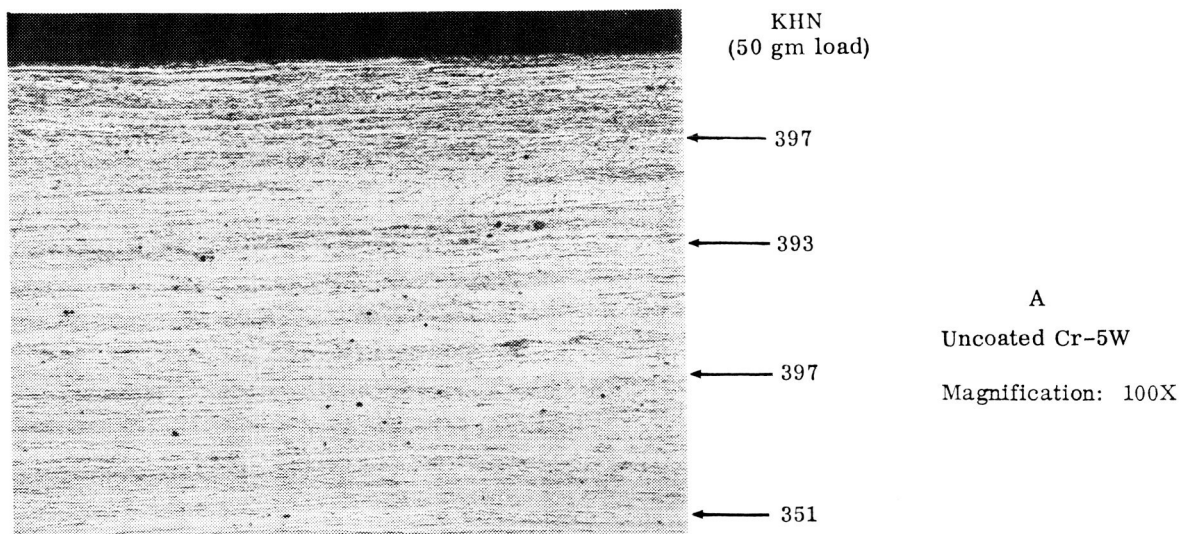


FIGURE 17. INTERSTITIAL SINK STUDY OF UNCOATED Cr-5W ALLOY;  
As-Bonded (Cr-5W)-V, and As-Bonded (Cr-5W)-V-Ti Composites

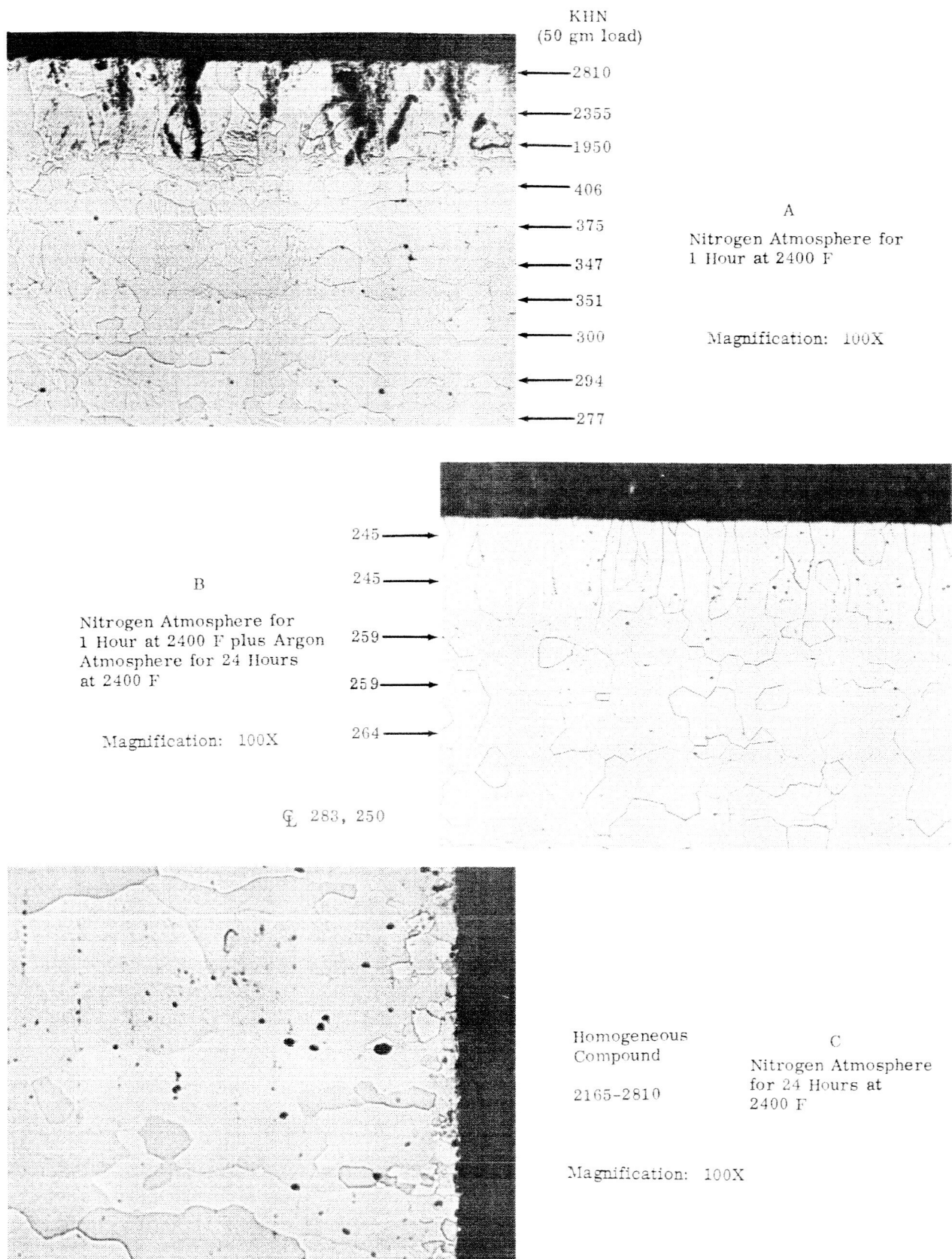


FIGURE 18. INTERSTITIAL SINK STUDY OF Cr-5W ALLOY; Exposed to Nitrogen and Homogenized in Argon

TABLE V  
VACUUM FUSION ANALYSES FOR O<sub>2</sub> AND N<sub>2</sub> IN V, Ti, AND V-Ti SINK LAYERS  
(Removed from Cr-5W Substrate)

2400 F Exposure Time (hr)	V		Ti		V-Ti	
	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)	O <sub>2</sub> (Wt%)	N <sub>2</sub> (Wt%)
0	0.138 to 0.190	0.033 to 0.046	0.127 to 0.416	0.033 to 0.039	0.047	0.0012
96	0.643	17.6	0.049 to 0.25	17.6 to 18.2	0.185 to 0.560	0.841 to 1.73

The vacuum fusion analysis values for the substrate nitrogen content (Table IV) appeared to be low, since cubic CrN of stoichiometric composition contains 21 to 22 weight-percent nitrogen and hexagonal Cr<sub>2</sub>N exists over the range 9.3 to 11.9 weight-percent nitrogen.

To obtain positive identification, a powder sample was taken for X-ray diffraction analysis, and additional chemical analyses were performed using the micro-Kjeldahl technique. By the Kjeldahl method, the 24-hour sample showed 10.6 weight-percent N<sub>2</sub>, while the 96-hour sample showed a value of 11.4 weight-percent. X-ray diffraction on the 24-hour sample showed it to be predominantly hexagonal Cr<sub>2</sub>N, with the three strongest reflections occurring for d-values of 2.11, 2.39, and 2.23Å, but some reflections corresponding to cubic CrN and free chromium were also recorded.

The structures obtained with (Cr-5W)-V and (Cr-5W)-V-Ti after a one-hour exposure at 2400 F are shown in Figures 19 and 20. Both formed an outer nitride layer (VN and TiN), but, whereas TiN appeared to be an effective nitrogen barrier, nitrogen diffused through the VN and contiguous V<sub>2</sub>N layers to form a V-N solid solution. No nitrides were formed in the chromium alloy in either case.

Homogenization annealing in argon (very low partial pressure of N<sub>2</sub>) caused the VN to dissociate forming the twinned body centered tetragonal phase reported by Rostoker (Ref. 5) which contains about 5 weight-percent N<sub>2</sub>, while the TiN phase is evidently more stable (Fig. 21 and 22). The VN layer could lose nitrogen by diffusion inward and by dissociation, but since its dissociation pressure is orders of magnitude higher than the partial pressure of N<sub>2</sub> in gettered argon, the loss is more likely to be by the latter mechanism. These observations agree well with reported values for the free energies of formation (Ref. 6 and Fig. 23) of VN (-10K cal/gm mole at 2400 F)

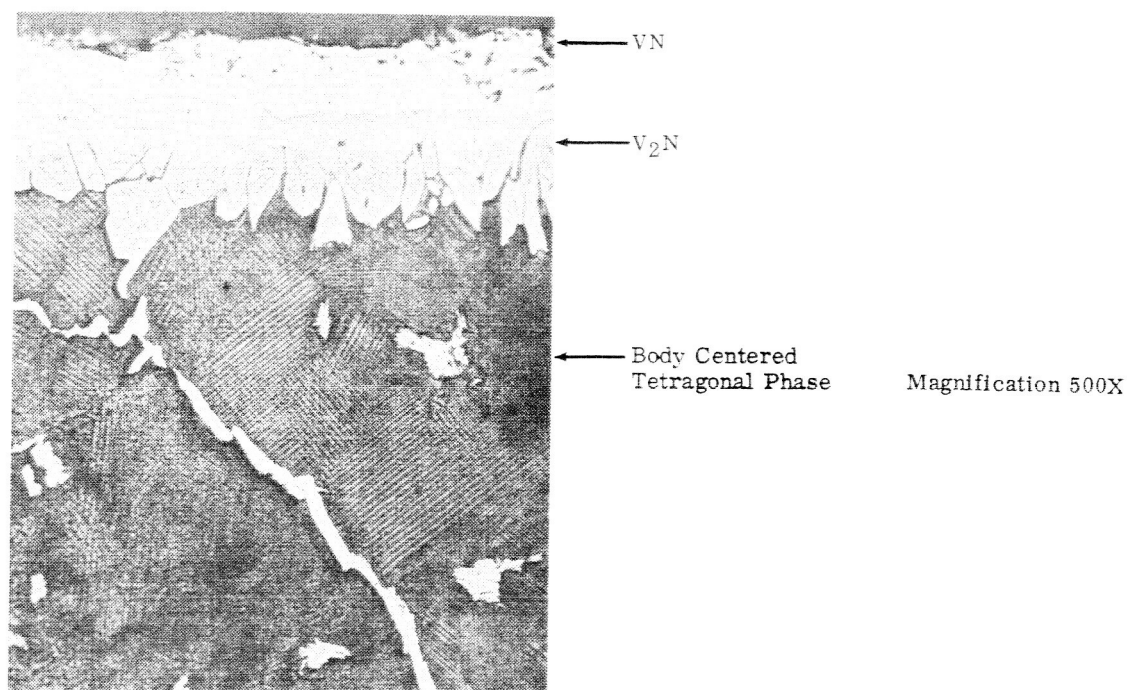
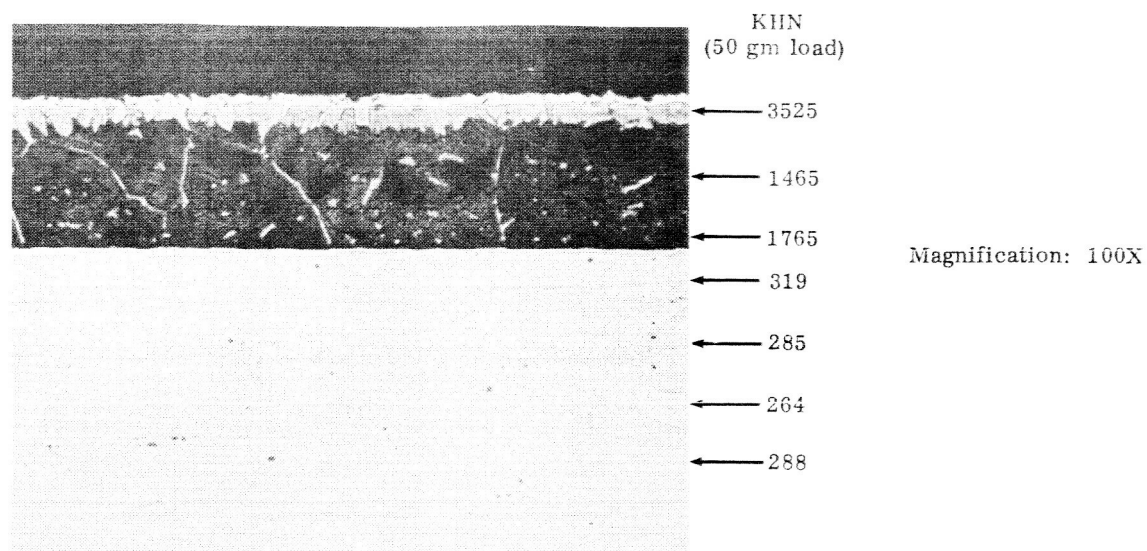


FIGURE 19. INTERSTITIAL SINK STUDY OF (Cr-5W)-V COMPOSITE;  
Exposed to Nitrogen for 1 Hour at 2400 F



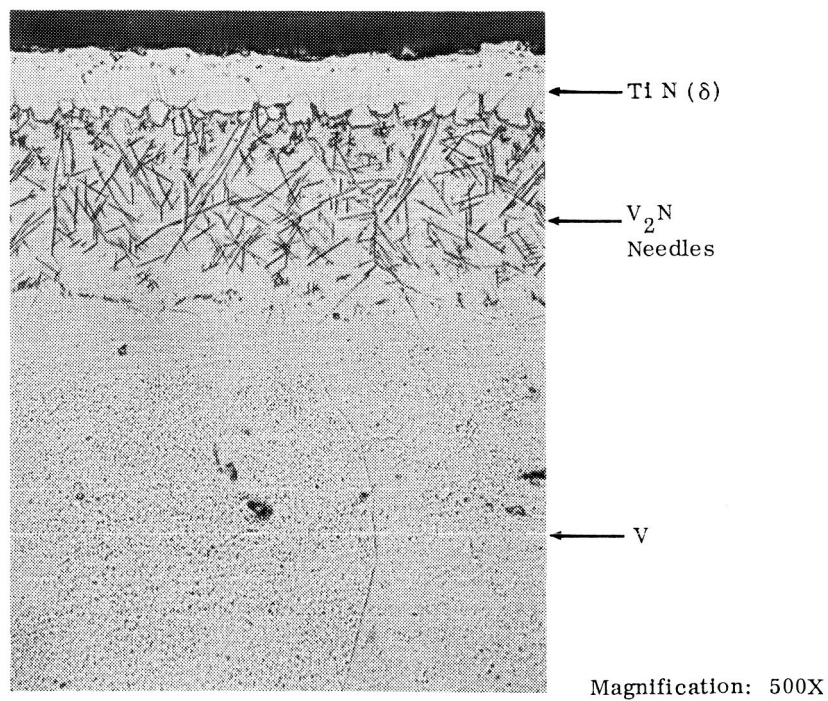
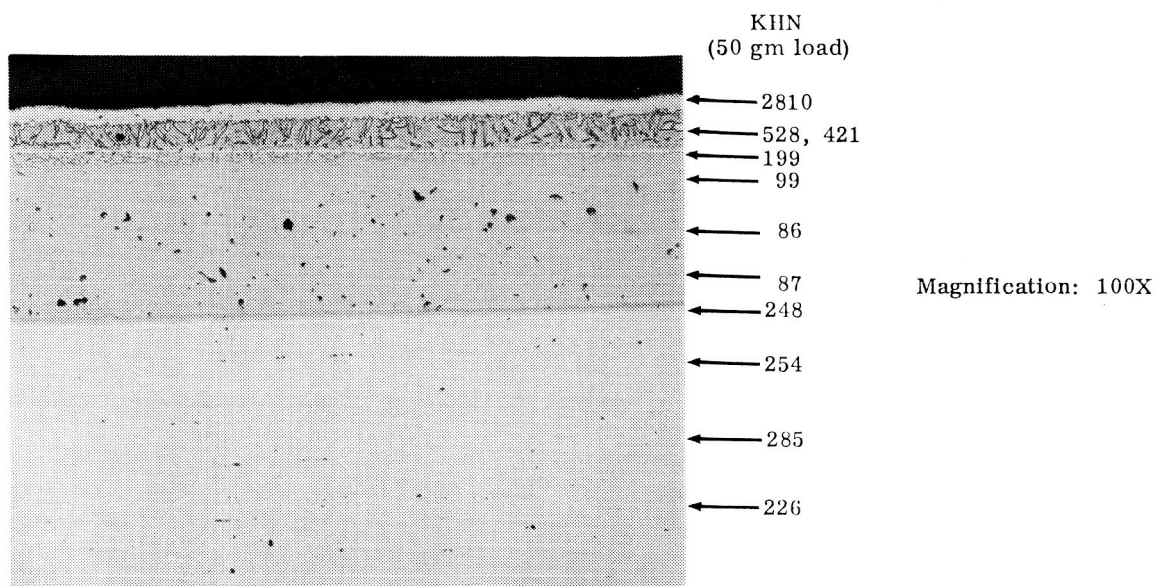


FIGURE 20. INTERSTITIAL SINK STUDY OF (Cr-5W)-V-Ti COMPOSITE;  
Exposed to Nitrogen for 1 Hour at 2400 F

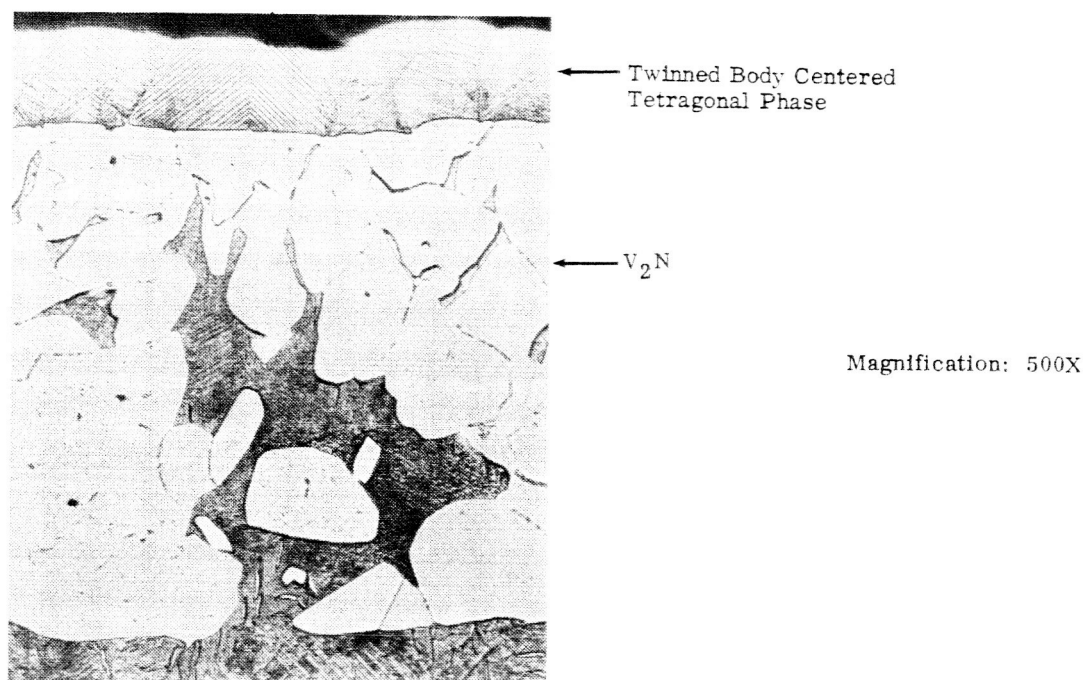
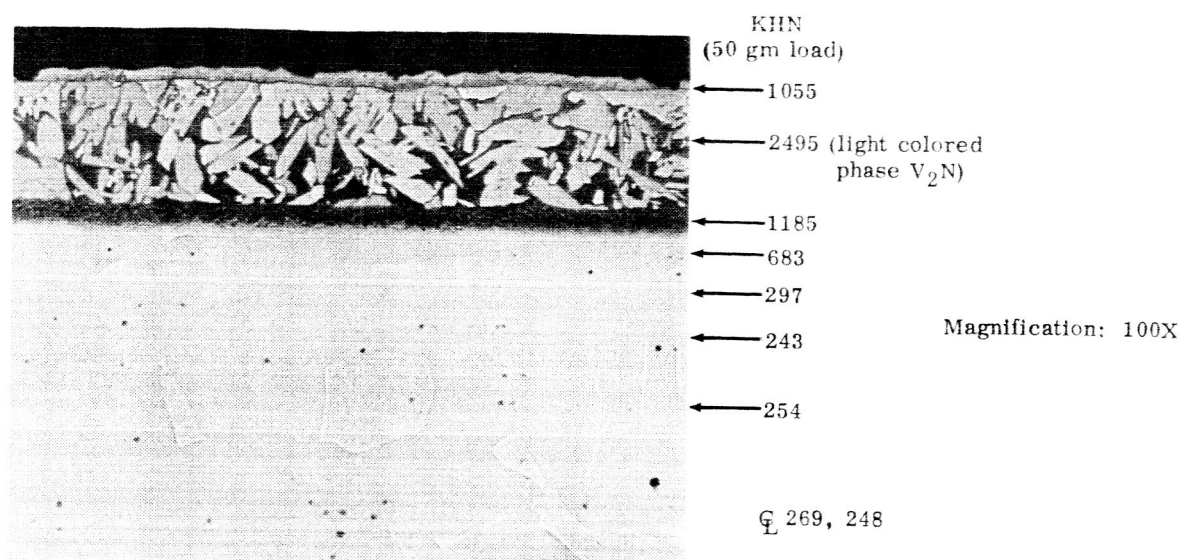


FIGURE 21. INTERSTITIAL SINK STUDY OF (Cr-5W)-V COMPOSITE;  
Exposed to Nitrogen for 1 Hour at 2400 F and Annealed in  
Argon for 24 Hours at 2400 F



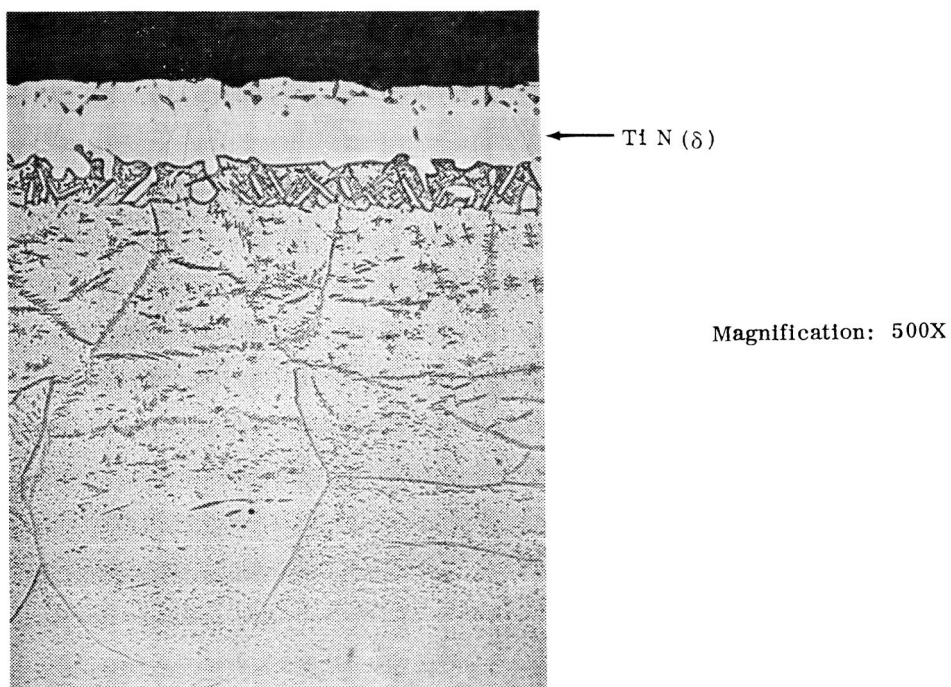
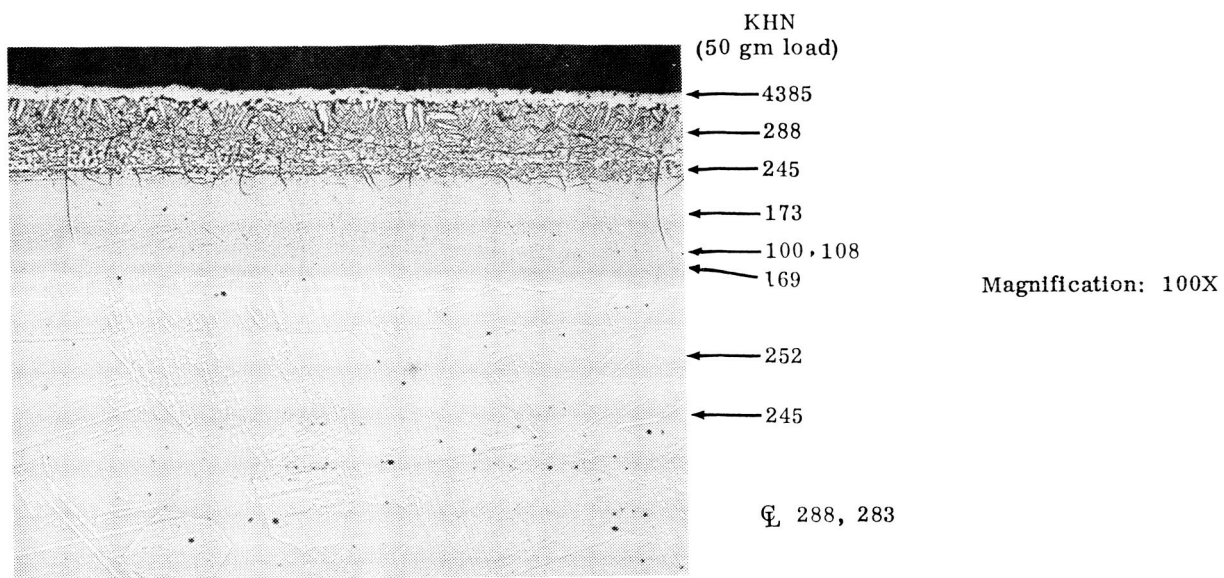


FIGURE 22. INTERSTITIAL SINK STUDIES OF (Cr-5W)-V-Ti COMPOSITE;  
Exposed to Nitrogen for 1 Hour at 2400 F and Annealed in  
Argon for 24 Hours at 2400 F

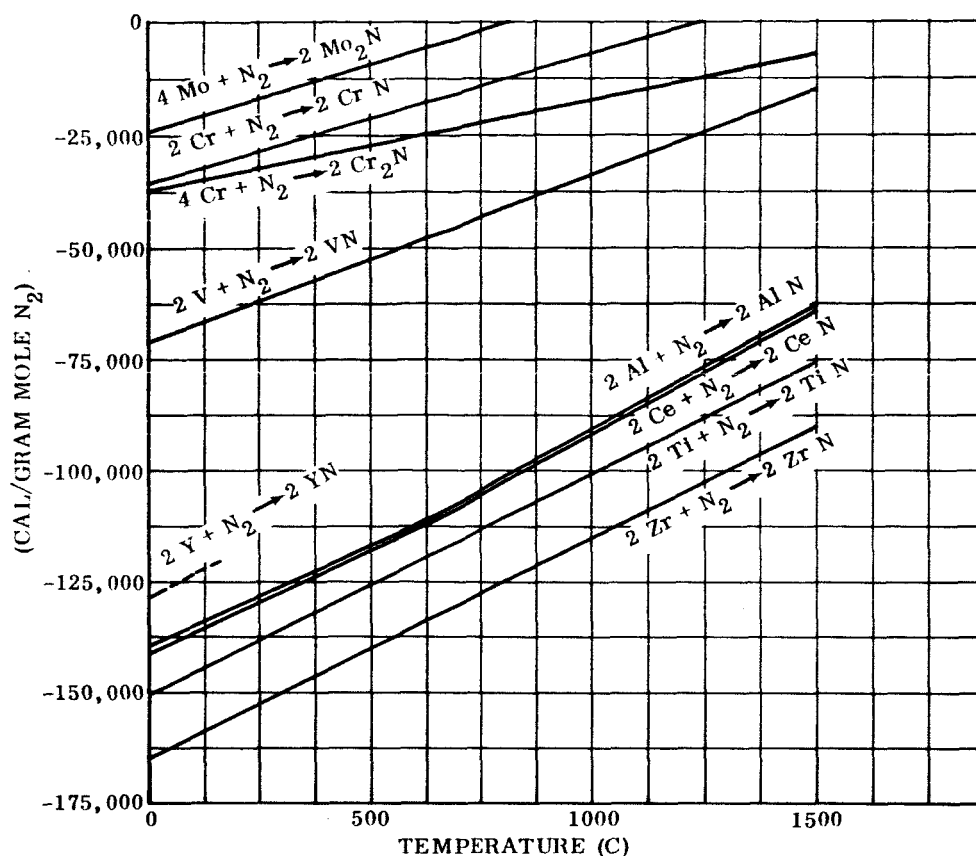


FIGURE 23. FREE ENERGY OF FORMATION OF NITRIDE

and TiN ( $-45\text{K cal/gm mole}$  at  $2400\text{ F}$ ). Very low nitrogen values for the chromium alloy substrate were recorded in each case (Table V), and the very low hardness of the vanadium layer with titanium present serves to illustrate the powerful sink effect of titanium which removed interstitials from the vanadium layer. With 4- and 24-hour exposures, little change occurred in the (Cr-5W)-V-Ti samples, while the (Cr-5W)-V samples showed a progressive increase in thickness of the VN layer. No grain boundary or needle-like precipitation of  $\text{Cr}_2\text{N}$  occurred in any of these specimens and no increase in the microhardness of the substrate was observed. The specimens with the V and V-Ti sinks are shown in Figure 24 after 96 hours exposure to nitrogen. All the vanadium layer (Fig. 24A) was converted to VN, and  $\text{Cr}_2\text{N}$  had formed (probably  $(\text{VCr})_2\text{N}$ , since both subnitrides are hexagonal) at the original interface. Considerable diffusion of nitrogen into the chromium had occurred, with grain boundary and intra-granular (needles) precipitation of nitride. An interesting observation brought out by Figure 24A is that formation of nitride needles in the chromium alloy matrix requires the condition of slow arrival rate of nitrogen atoms which can be brought about by low

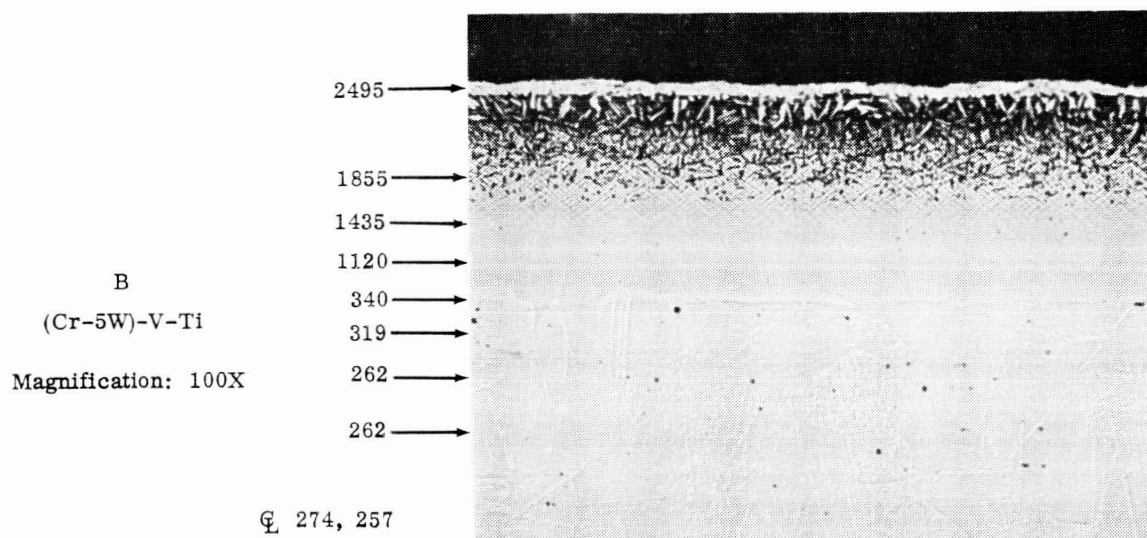
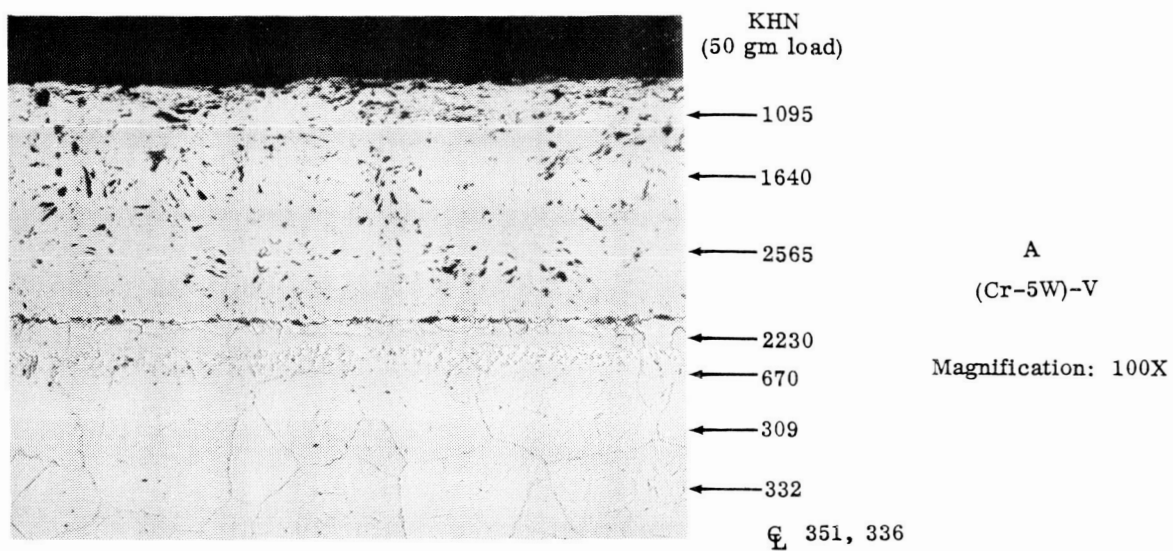
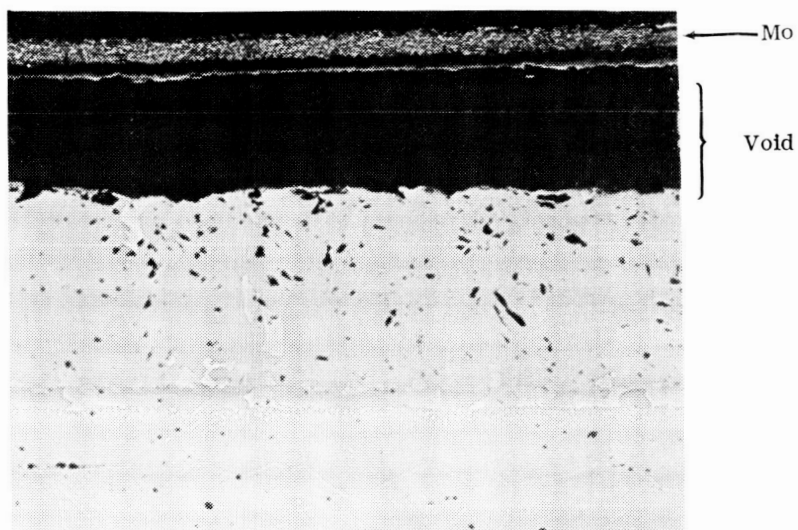


FIGURE 24. INTERSTITIAL SINK STUDIES OF (Cr-5W)-V AND (Cr-5W)-V-Ti COMPOSITES; Exposed to Nitrogen for 96 Hours at 2400 F

partial pressures of nitrogen or the presence of a partial diffusion barrier. Lower temperatures (hence slow diffusion rates) would favor nitride needle formation. The effectiveness of  $\delta\text{TiN}$  as a nitrogen diffusion barrier is shown in Figure 24B. Formation of vanadium nitrides occurred only when all of the titanium layer had been transformed. Twinned V-N solid solution was formed down to about 0.007-inch of the original vanadium thickness, but a relatively soft and ductile vanadium or vanadium-chromium layer remained between the nitrified layer and the chromium substrate. The substrate chromium alloy had low hardness values below the vanadium diffusion layer and showed no signs of nitride precipitation. Vacuum fusion analysis indicated less than 20 ppm of nitrogen.

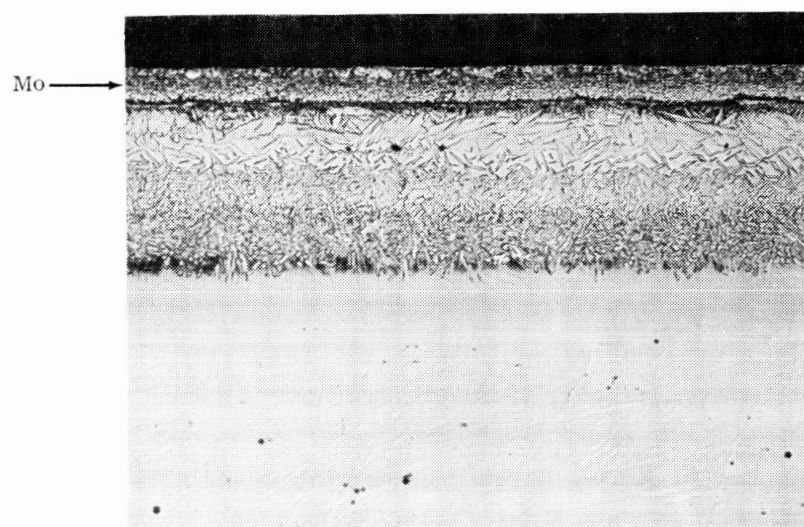
It was anticipated that molybdenum would act at least as a moderately good diffusion barrier because of low solubility for nitrogen and a positive (extrapolated) free energy of formation of  $\text{Mo}_2\text{N}$  (approximately 15 K cal/gm mole). The nitrogen diffusion studies, however, showed that at 2400 F molybdenum was quite ineffective as a diffusion barrier and that nitrogen appeared to diffuse rapidly through the molybdenum grain boundaries. The Cr-V-Mo and Cr-V-Ti-Mo composites after 96 hours exposure to nitrogen at 2400 F are shown in Figure 25. With molybdenum bonded directly to the vanadium sink, all of the sink layer was converted to VN and the metallic molybdenum parted from this compound layer during metallographic preparation. With molybdenum bonded to titanium, a metallic bond was preserved, since a continuous  $\delta\text{TiN}$  layer was not formed. The fact that a nitrogen diffusion barrier of TiN did not form is probably accounted for by the alloying between the rapidly diffusing titanium and molybdenum and the diffusion rate of nitrogen through the alloy. Vacuum fusion analyses for nitrogen (Table IV) of the Cr-5W substrate showed extremely low values for the Cr-V-Ti-Mo sample (5 ppm) while some substrate contamination had occurred in the Cr-V-Mo composite. Table V shows vacuum fusion analysis values on vanadium, titanium, and vanadium-titanium sink layers after 96-hour sample exposure to nitrogen, and serves to identify the compounds at VN and TiN, respectively. The value of 0.84 to 1.73 weight-percent nitrogen obtained on the V-Ti layer (Fig. 24B) would seem to be a reasonable average for a 0.001-inch layer of TiN in contact with vanadium-titanium-nitrogen alloy.

The purpose of these experiments was to evaluate the validity of the interstitial sink concept when applied to a specific coating system. The experimental conditions differ from actual test conditions in two major respects. First, an outer silicide barrier was not present which allowed much higher nitriding rates than would be



A  
(Cr-5W)-V-Mo

Magnification: 100X



B  
(Cr-5W)-V-Ti-Mo

Magnification: 100X

FIGURE 25. INTERSTITIAL SINK STUDIES OF (Cr-5W)-V-Mo AND (Cr-5W)-V-Ti-Mo COMPOSITES; Exposed to Nitrogen for 96 Hours at 2400 F

encountered in a coating system and which would probably affect the kinetics of nitride formation; and second, pure, gettered nitrogen was used to avoid the complications which would have been associated with phase identification if oxygen had been present.

However, these experiments clearly illustrate the strong nitrogen sink effect of both vanadium and vanadium-titanium when in contact with chromium, and show that nitrogen contamination of the chromium substrate did not occur until all of the vanadium layer was converted to  $V_2N$ . This is in complete agreement with theoretical predictions based on thermodynamic data. With the presence of a stable, outer silicide oxygen/nitrogen barrier, a vanadium or vanadium-titanium alloy sublayer would thus be expected to act as an effective reservoir for any nitrogen which might bleed through microcracks in the silicide.

# 4

## COATING PROCESS DEVELOPMENT

At the onset of this program, no major coating development was anticipated except to adapt known coating processes to the Cr-5W alloy substrate. As the program progressed, however, major laboratory effort was required to apply rhenium and vanadium to the substrate. With rhenium, both chemical vapor deposition and aqueous deposition were investigated; with vanadium, nonelectrolytic and electrolytic fused salt deposition and high- and low-pressure pack depositions were studied. In the pack process, activator, retort material, and process temperature were extensively studied due to the sensitivity of the process to these variables. No major development was required in the application of titanium, molybdenum, or silicon.

The materials used are generally discussed in each section. An overall summary of material purity and sources is presented in Appendix II.

### 4.1 THE Re-(Ti, Cr, V)-Si SYSTEM

In 1934, Fink and Deren (Ref. 7 and 8) reported bright, mirror rhenium surfaces deposited from a potassium perrhenate - sulfuric acid bath. The deposits were produced at current densities around 10.8 amp/sq dm (100 amp/sq ft) in room temperature baths at a pH of 0.3 to 3.0. The recommended pH was  $1.0 \pm 0.1$ . In 1936, Young (Ref. 9), in essence, reproduced the previous work and also reported hard and bright rhenium deposits. Young postulated that the brittleness was due to hydrogen in the plate. This brittleness was eliminated by an underlay of rhodium plate which increased the overvoltage of hydrogen and, reportedly, aided deposition of the rhenium metal. In 1949, Netherton and Holt (Ref. 10) reported that the sulfate bath was most satisfactory and also reported studies with citrate plating baths. In 1951 (Ref. 11) and 1952 (Ref. 12), these same authors reported electrodeposited rhenium alloys containing up to 85 percent rhenium with iron, cobalt, or nickel from ammoniacal-citrate baths. Levy (Ref. 13) reported in 1951 that rhenium, 0.001 to 0.003 inch in thickness, was plated on platinum, rhodium, chromium, and nickel from a potassium perrhenate solution in concentrated sulfuric acid. The thickness was attained by depositing

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TABLE VI  
PLATING DATA USING POTASSIUM PERRHENATE BATH AND CURRENT  
DENSITY OF 15 amp/dm<sup>2</sup>

Cr-5W Alloy Sample (0.25 in. by 0.25 in. by 0.080 in.)											
Sample Number	Bath Variables				After Plating				After outgassing in H <sub>2</sub> atmosphere at 950 C for 15 minutes		
	Temperature (C)	Time (min)	pH	Agitation	Weight Change (gm)	Thickness (mil)	Appearance	Heating Rate to 950 F	Weight Change (gm)	$\Delta t$ (mil)	Appearance
8	29 (Room)	60	1.0	No	+0.0015	0.25	Porous	Fast	Nil	-0.1	Discontinuous and deposit only at few places
9	29 (Room)	60	1.0	No	+0.0073	0.4	Good coating but not completely continuous	Not H <sub>2</sub> fired.			
10	77	60	1.0	No	+0.0065	0.15	Porous	Fast	-0.0005	-0.15	Coating flaky - not adherent and discontinuous
11	75	30	1.0	No	+0.0054	0.4	Porous	Fast	-0.0004	-0.25	Coating flaky - not adherent and discontinuous
12	75	30	1.0	No	+0.0058	0.25	Continuous coating (porous) but not of uniform thickness	Not H <sub>2</sub> fired.			
13	45	60	1.0	No	+0.0046	0.2	Porous	Fast	-0.0004	-0.05	Coating flaky and discontinuous
14	45	60	1.0	No	+0.0043	Nil	Porous	Not H <sub>2</sub> fired.			
18	75	30	1.8	Yes	+0.0035	0.25		Slow	--	--	Flaky but thick deposits



successive layers and heating the individual deposits at 1000 C to change the deposit from the amorphous to the crystalline state. Work at Battelle in 1952 by Sims and others (Ref. 14) indicated an improvement in rhenium deposition using a plating bath composed of ammonium perrhenate and sulfuric acid at a pH of 1.0 to 1.3. The best plates were obtained by plating for 6 minutes at room temperature with a current density of 10.8 amp/dm<sup>2</sup> (100 amp/sq ft). Specimens were then fired in hydrogen from 900 to 950 C for 15 minutes to reduce any rhenium oxide that was present in the plate. This plating cycle was repeated several times. Two cycles produced a plate about 0.001 inch thick (Ref. 14). Specimens plated and hydrogen-fired remained bright after long exposure in air. As-plated specimens, exposed to ambient laboratory atmospheres, however, oxidized in a short time.

#### 4.1.1 Aqueous Rhenium Deposition

Based on the above literature survey and past experience at Solar, the following plating solution was prepared:

- Potassium perrhenate (KReO<sub>4</sub>) = 17.5 gm/l
- Concentrated H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84) = 90 gm/l
- Ammonium hydroxide (28.9 NH<sub>3</sub>) = 100 cc/l
- Current density 10 to 16 amp/dm<sup>2</sup>

Variables studied were:

- Bath temperature - room temperature, 45 C, and 75 C
- Plating time - 30 and 60 minutes
- Agitation
- Outgassing
- pH (normally 0.80 to 1.0)

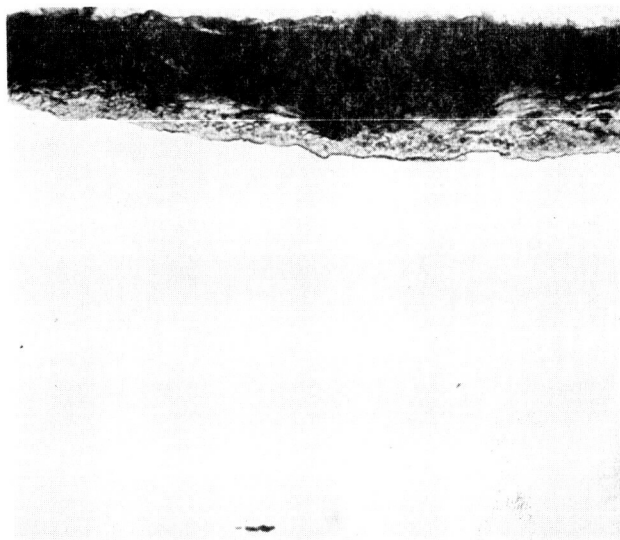
Specimens were cleaned either by electrolytic etching in 50 percent HCl and 50 percent H<sub>2</sub>O, or 10 percent oxalic acid and 90 percent H<sub>2</sub>O followed by distilled water rinsing and argon drying. A platinum anode and a Harrison constant current supply were used for all experiments.

Data on rhenium plating are given in Table VI, and photomicrographs of Cr-5W specimens are shown in Figure 26.

The as-deposited rhenium plates were relatively bright, but hydrogen bubbles were found to cling to the plate which produced significant void areas. A mechanical

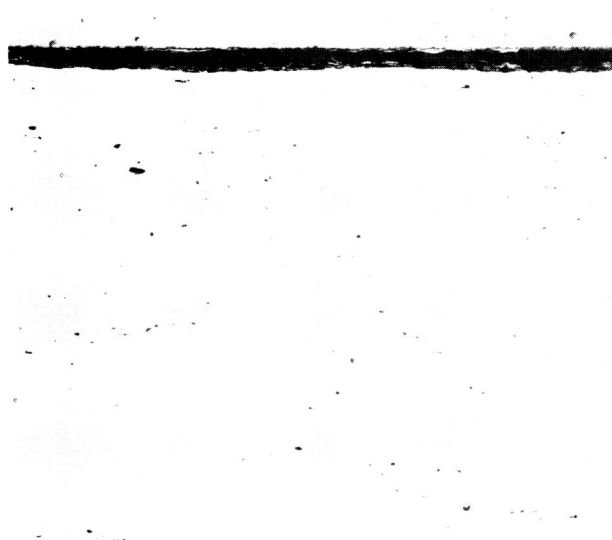


Magnification: 100X



Magnification: 500X

A. As-plated Specimen No. 12



Magnification: 100X



Magnification: 500X

B. Specimen No. 11 After  $H_2$  Firing at 950 C for 15 Minutes (outgassing)

FIGURE 26. RHENIUM-PLATED Cr-5W SPECIMENS; Potassium Perrhenate Bath at 75 C for 30 Minutes , Current Density of 15 Amp/dm<sup>2</sup>, and a pH of 1.0

vibrator attached to the cathode produced a significant decrease in the void areas. Deposition at 75 C produce the thickest most uniform deposits (0.0005 inch in 30 minutes).

The as-deposited rhenium plate has an amorphous structure. Hydrogen annealing was believed to be necessary to reduce any rhenium or chromium oxide to the metal and to remove all chemically combined or absorbed hydrogen. Initially, very rapid heating to 950 C (10 minutes) was used. Metallographic examinations of the deposits after annealing showed almost complete lack of bonding of the plate to the chromium. The problem was thought to be the result of the disruption of the bond by evolution of hydrogen. Slow heating to 950 C (4 hours to temperature) was tried and found to improve plate continuity, but all plates observed showed some discontinuity. Double-plating and double-firing were evaluated to determine the effect on coating continuity but the coatings were only slightly improved.

Preliminary experiments in a plating solution of the above composition adjusted to pH of 1.8 and held at 75 C produced the most uniform coating appearance as deposited.

Ammonium perrhenate solution was evaluated since the ammonium salt has 3 times greater solubility than potassium perrhenate. The plating solution provided increased deposition rates, but the problem of obtaining a dense, continuous coating is associated with the nature of the electrodeposited material itself. Conversion of the sponge like deposit to 100 percent dense metal resulted in a 20 percent shrinkage which could not be accommodated without breaking the plate. At best, a discontinuous flake-like coating of rhenium was obtained after firing.

The effect of firing under hydrogen or in a vacuum at 950 C was investigated. It was found that annealing in a vacuum of  $10^{-6}$  Torr did not produce a more adherent rhenium coating; but rather, seemed to result in a greater loss due to flaking off from the chromium substrate. These results showed that without major development, aqueous deposition of rhenium was unsuitable as a technique for the production of a diffusion barrier coating.

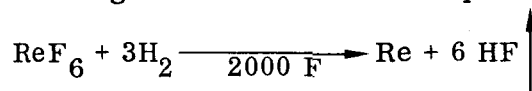
#### 4.1.2 Chemical Vapor Deposition

The San Fernando Laboratory (SFL) was chosen as the subcontractor for rhenium plating by the chemical vapor deposition technique. This laboratory is probably the most experienced organization in the nation in the deposition of this element.

Ten, 5-gram, arc-melted buttons were sent to SFL for application of a 0.001- to 0.002-inch coating of rhenium. A wire was welded to each button to suspend it in the deposition chamber. The samples were coated by thermal decomposition of a rhenium chloride gas at 2200 F.

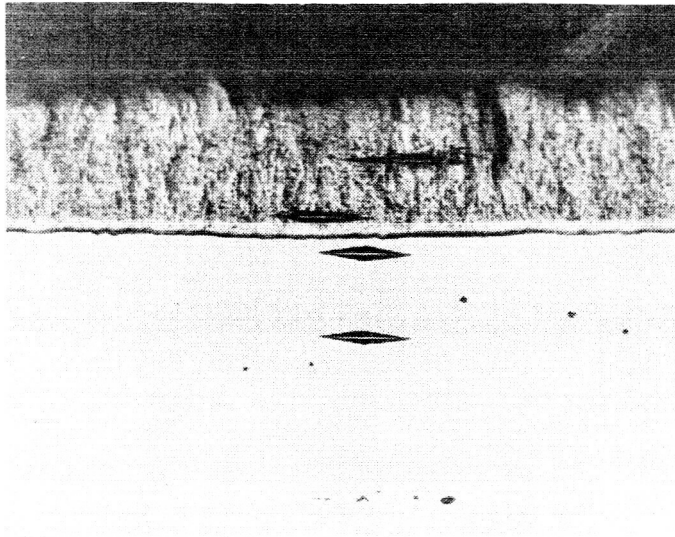
The rhenium layer was inconsistent in thickness (0.002 to 0.004 inch) and quality, and varied over the surface of each button, in addition to the variation from sample to sample. Of the ten buttons coated, only two exhibited continuous rhenium coating. The other eight samples were corroded by the chloride. The coated samples when examined metallographically revealed a secondary phase under the rhenium coating of thickness comparable to the rhenium. In one sample, the layer under the rhenium was very hard (KHN of 1300). In the other sample, the sublayer hardness was similar to the chromium (KHN of 120 to 170). These layers are attributed to surface contamination of the chromium during coating.

An additional study was conducted by SFL to investigate the rhenium vapor deposition from the rhenium fluoride. The fluoride process involved hydrogen reduction rather than halogen dissociation. The equation for the reaction is:



The hydrogen reduction was expected to minimize the corrosion of the specimens.

Three samples (0.5 by 1.0 by 0.060 inch) were submitted to SFL for rhenium coating by this process. Of the three specimens, one coating was continuous but developed a flow pattern from nonuniform contact of the gas stream and metal. This coating also blistered upon cooling indicating unsatisfactory bonding to the chromium. Another sample was coated at a higher temperature. The deposit was nonuniform and indicated loss of substrate material either by chemical reaction or vaporization. The third sample was coated satisfactorily by applying a basic coat at approximately 1800 F after which the temperature was raised to approximately 2200 F to complete the deposition and facilitate a bond. This coating was acceptably smooth (Fig. 27) and continuous, although somewhat spongy with the deposit varying from 0.003 inch on the surface to 0.006 inch on the edges. No secondary phase was observed in the chromium adjacent to the rhenium. The hardness in the substrate was within the normal hardness range for this chromium alloy.



Magnification: 250X

FIGURE 27.

RHENIUM CHEMICALLY VAPOR  
DEPOSITED ON Cr-5W ALLOY

#### 4.1.3 Potential of Developing Rhenium Coatings for Chromium Alloys

The development of the coatings utilizing a rhenium-base requires the deposition of this element (with a metallurgical quality bond) to the substrate without introducing significant substrate or coating embrittlement.

Electroplating of rhenium from aqueous solution shows little potential for providing an adherent coating capable of being heated to elevated temperature, without extensive further development.

The deposition of rhenium on chromium chemical vapor deposition shows a definite potential but also appears to require a development program. The most serious limitation of this process is due to extreme sensitivity to temperature and gas-metal contact. Even in small test specimens, the coating varied in thickness by a factor of two from edge to center. Slight turbulence in the gas flow produced a rippled deposit. These problems, potentially soluble for test specimens, seem very serious for large or complex components.

At the recommendation of NASA project personnel, work on the rhenium-titanium-chromium-silicon system was discontinued because of the extensive research required in the application of rhenium.

## 4.2 THE (V, Ti, Mo)-Si SYSTEM

### 4.2.1 Vanadium Deposition - Fused Salt Process

It is generally agreed that vanadium can not be deposited in coherent form from aqueous systems.

Vanadium has been electrorefined by Baker and Ramsdell (Ref. 15) from a fused salt bath ( $\text{NaCl-VCl}_2$ ). In 1964 Mellors and Senderoff (Ref. 16) described a general process which included the electrodeposition of vanadium from fused salt. The coatings were described as thick, coherent, 100 percent dense, of high purity, and surprisingly smooth.

The deposition of coatings from a fused salt bath combines the desirable features of plating at high temperatures to produce a good bond to the substrate and at the same time produce a high-purity coating. Both electrolytic and nonelectrolytic deposition processes were investigated. The electrolytic process has the advantage of being free from diffusion as a driving mechanism for deposition, but the process has limited throwing power. The nonelectrolytic process is conversely limited by diffusion rates and has relatively good throwing power.

#### Fused Salt Electrodeposition of Vanadium

In view of its potential advantages, i.e., the relatively low process temperature of 1900 F which obviates problems of chromium vaporization and the high deposition rates, the first process investigated to deposit the vanadium sublayer was electrolytic fused salt. Based upon related work at Solar in depositing vanadium upon other metal substrates, the following bath and process parameters were selected:

- |                          |  |
|--------------------------|--|
| • Bath composition (wt%) | NaF - 70 percent (solvent)<br>$\text{K}_2\text{VF}_5$ - 15 percent (active metal)<br>Vanadium (granules) - 15 percent (active metal) |
| • Bath temperature       | 1900 F   |
| • Bath voltage           | 0.25 volt  |
| • Current density        | 78 ma/cm <sup>2</sup>  |
| • Process time           | 5 hours  |

A schematic diagram of a fused salt plating cell is shown in Figure 28.



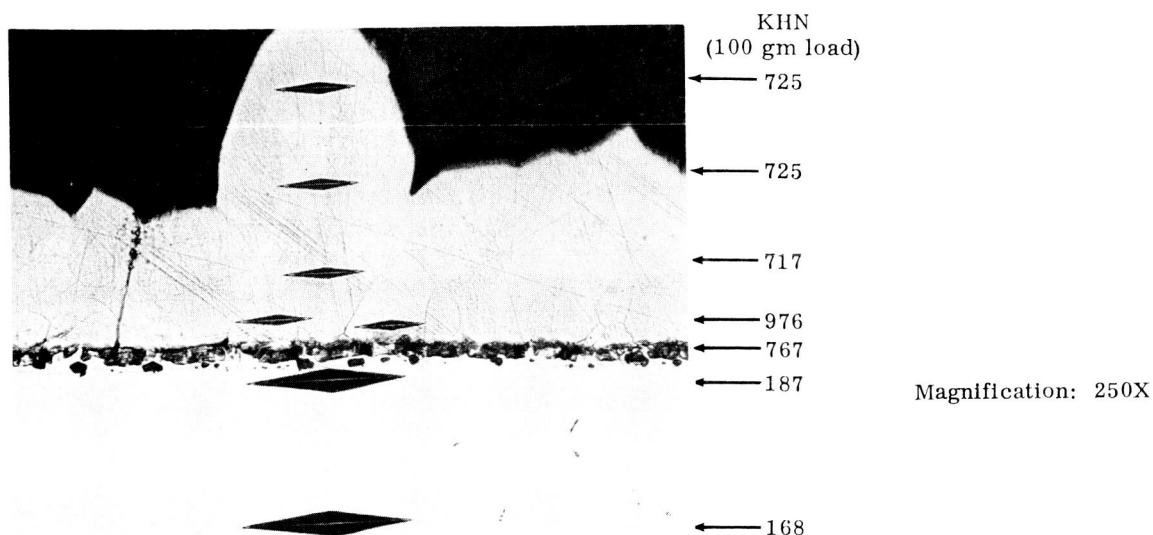


FIGURE 29. VANADIUM DEPOSITION BY ELECTROLYTIC FUSED SALT PROCESS AT 1900 F FOR 5 HOURS

To investigate the feasibility of reducing the interstitial element levels by gettering the fused salt electrolyte, the salt bath was reduced at 1900 to 2000 F using vanadium sponge and titanium wire. Vanadium deposits on chromium softer than a KHN of 700 could not be produced, although the thickness of the vanadium coating was 0.004 to 0.005 inch. Therefore, it was decided (with the sponsor's approval) to suspend work on the electrolytic fused salt processes for vanadium deposition since development of the process would require more time than the results warranted.

#### Nonelectrolytic Deposition

In view of the problems encountered in attempts to produce a smooth coating by electrolytic vanadium deposition and pack processes, nonelectrolytic deposition was investigated. Based upon related work at Solar in depositing vanadium upon other metal substrates, the following bath and process parameters were selected:

- Bath composition (wt%)
  - 60 LiF-40NaF - 85 percent (solvent)
  - $K_3VF_6$  - 15 percent (active salt)
  - V granules - 50 percent of V content in active salt
- Anode
  - V pressed granular cylinder
- Bath temperature
  - 2000 F



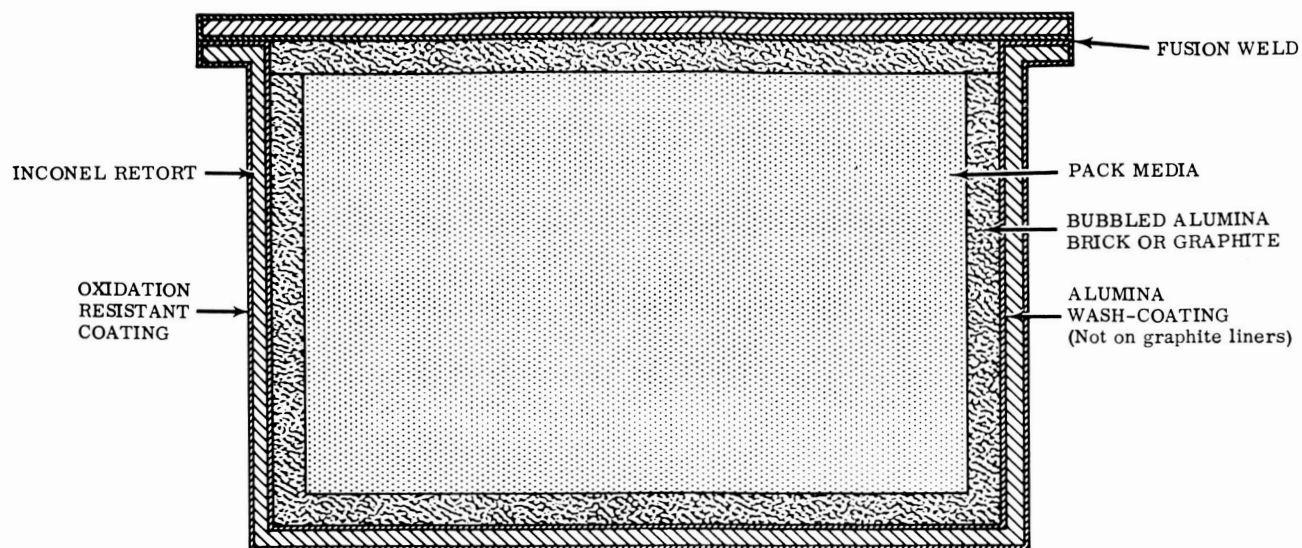
Care was taken in the synthesis of the  $K_3VF_6$  and in the preparation of the bath to guarantee that the system was free of oxides or moisture. The bath was heated in purified argon to 2000 F and equilibrated with the vanadium for 24 hours. The equilibrated bath was electrolyzed with a D36 columbium alloy cathode. The resulting bath was tested for effectiveness for vanadium nonelectrolytic plating. The bath was found to produce a fairly smooth deposit on the Cr-5W samples at the rate of 0.0005 to 0.001 inch in 24 hours at 2000 F. Microscopic examination showed that these coatings were nodular where the thickness exceeded 0.0003 inch. The coating hardness for the vanadium layer was 200 to 250 KHN. The chromium substrate showed no effects of bath corrosion. The purity of the coating was excellent, but the thickness was nonuniform and the deposition rate was too slow to be of interest.

The fused salt electroless deposition of vanadium shows a potential but would require an extensive developmental program.

#### 4.2.2 Vanadium Deposition - Pack Processes

Difficulties encountered in the deposition of vanadium by the fused salt process early in the program led to an evaluation and development of the originally proposed backup technique, the halide pack process.

Packs are a very convenient chemical reactor in which chemicals can be generated and decomposed to effect metal transfer to the parts being coated. The entire complex series of reactions occurring within packs can be looked upon as non-equilibrium because the driving mechanism of deposition is primarily the concentration gradient rather than chemical equilibrium. The variables that can be introduced into packs are almost unlimited. The active metal or silicon can constitute 100 percent of the pack or as little as 5 percent. The halide activator concentration is usually not critical, and can vary from 0 to 10 percent. Temperature is limited only by the type of retort and method of heating, and can be as high as 2600 F with current processes using refractory metal or graphite retorts. Pressure in the retort can vary from 0.5 to 800 Torr, but the practical minimum pressure in most systems is the equilibrium vapor pressure of the halide activator.



Retort Cross Section

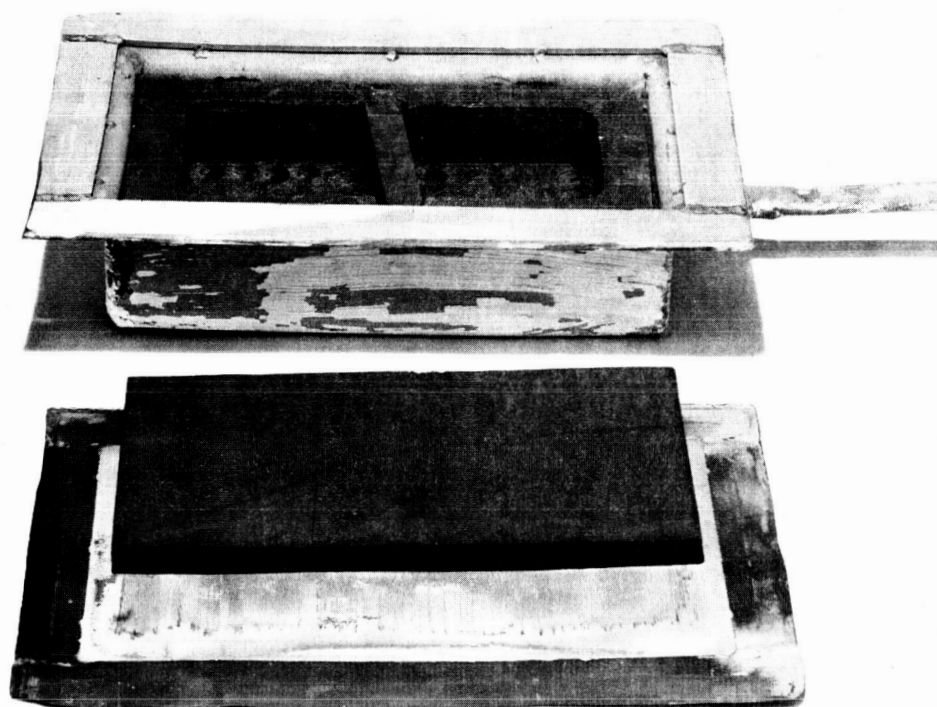


FIGURE 30. TYPICAL GRAPHITE-LINED INCONEL RETORT

Chronologically, the pack deposition experiments may be divided into two sections:

- Initial studies to select a suitable technique - these experiments being conducted mostly with arc-melted, pure chromium buttons since the program sheet alloy was not available at the commencement of the program
- Development and upscaling of the optimum process to allow satisfactory coating of large numbers of sheet specimens of the Cr-5W program alloy

This latter stage was hampered by the unavailability of vanadium sheet for retort construction. It was also found that in addition to the normal difficulty of vanadium plating (vanadium has proved to be one of the most troublesome elements to deposit), applying the process to chromium has its own special problems in terms of the high vapor pressure of chromium, and the similar  $\Delta F^\circ$  values of vanadium, tantalum, and chromium fluorides.

#### High Pressure Argon Pack Process

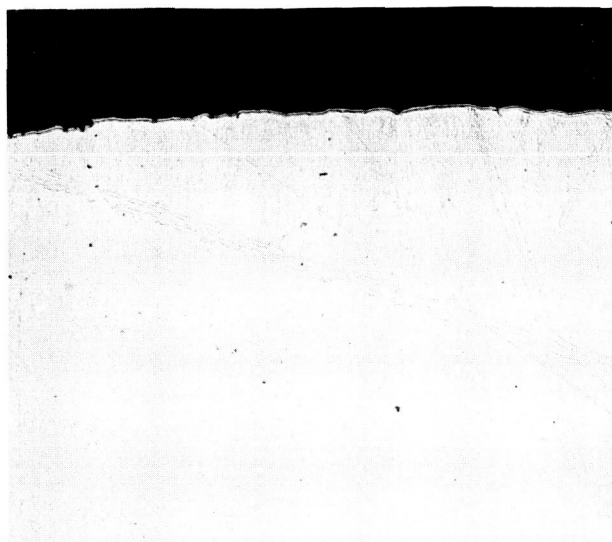
Solar's standard, graphite-lined, Inconel retorts were used initially in a series of experiments. A typical retort design is shown in Figure 30.

Control of atmosphere, cycle purging, and pressure in the retorts were accomplished through a single Inconel tube, 0.5 inch in diameter.

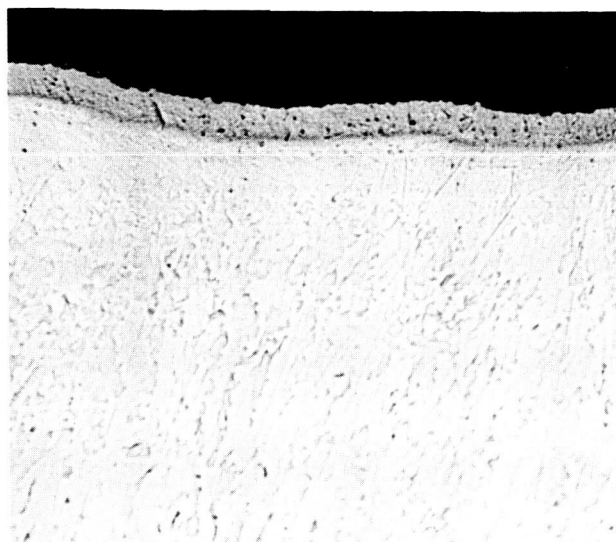
The cycle purge unit consists of a single 15 cfm Welch Duo-Seal mechanical vacuum pump with six separate mercury manometers and ducting systems to allow simultaneous evacuation, cycle purging, and pressure control of six retorts. Argon pressure and a mercury seal were used to maintain a positive pressure of approximately 800 Torr.

The initial pack consisted of vanadium granules of commercial purity (99.8 percent vanadium) to which was added NaF powder as the activator.

At activator levels of 0.1 and 1.0 weight-percent NaF and at a pack temperature of 2200 F for a run of 15 hours at 800 millimeters pressure of argon, the weight increase on chromium varied between 2 to 3 mg/cm<sup>2</sup> with negligible influence attributable to change in activator levels. Metallographic examination revealed a coating thickness of 0.00025 inch (Fig. 31). The X-ray fluorescence analysis of the pack coating indicated an alloy of vanadium and chromium with negligible pickup of iron, nickel, or potassium. The hardness of the pack coating was significantly lower (KHN of 303 - 50 gm load) than that of the fused salt coating, indicating that it was possible to achieve a soft vanadium-base coating which is essential for use as an interstitial sink.



Magnification: 100X



Magnification: 1000X

Thickness of Vanadium Deposit About 0.00025 inch. Weight Gain =  $2.5 \text{ mg/cm}^2$

FIGURE 31. VANADIUM DEPOSITION BY ARGON PACK PROCESS AT 2200 F FOR 15 HOURS

However, the quantity of vanadium deposited, measured by specimen weight gain, was of the order of 2 to 3  $\text{mg/cm}^2$  in contrast to the 31.0  $\text{mg/cm}^2$  for the desired 0.002-inch deposit of pure vanadium. In addition, the pack-produced coatings were frequently rough, sometimes discontinuous and variable in thickness (e.g., 0.00025 to 0.00050 inch).

To improve the pack conditions to favor a more rapid and uniform vanadium deposition and cleaner pack environment, the following process changes were made:

- An oil diffusion pump was employed for alternate pack evacuation and argon purge cycles, replacing a mechanical pump.
- Pure titanium foil was placed in a compartment adjacent to the pack to serve as a getter of residual gaseous contaminants in the argon/graphite environment.
- The entire pack was encapsulated in pure vanadium foil to minimize graphite involvement and to retain NaF and metal fluoride vapors within the pack for longer periods. In two cases, the graphite crucible was not included in the pack retort.
- The range of NaF activator level was increased to 1.0 to 3.3 percent to provide a larger reservoir of activator.
- Process temperatures were raised to 2250 and 2300 F to increase the diffusion rate of vanadium into the chromium substrate, which should have proved helpful if the deposition mechanism is essentially substrate diffusion controlled.

The actual results due to the process changes are listed in Table VII.

TABLE VII  
HIGH PRESSURE ARGON PACK DATA

Process Temperature (F)	Process Time (hr)	NaF Activator Level (%)	Change in Button Weight (mg/cm <sup>2</sup> )	Comments
2200	15	1.0	(+)2.5	Baseline for comparison
2200	15	0.1	(+)2.5-3.0	
2200	15	1.0	(+)1.0	
2250	15	1.0	(+)3.4	Graphite crucible removed from retort
2250	15	3.3	(+)5.2	
2300	15	1.0	0.0	

The effect of removing the graphite crucible from the retort, to counter suspected carbon involvement, was to reduce the quantity of vanadium deposited from 2.5 to 1.0 mg/cm<sup>2</sup> (2200 F). This reduction was possibly due to the larger effective pack volume (requiring more NaF to produce equilibrium pressures) and increased NaF vapor migration from the pack, characteristic of the almost empty retort with graphite removed. However, the lack of weight change under precisely the same pack condition at 2300 F indicated that a weight loss mechanism also was active, presumably increased chromium evaporation. Metallographic examination of the 2300 F specimen revealed the presence of a coating, suggesting that chromium losses had just balanced vanadium gains. Maximum weight gains were obtained at 2250 F, although the presence of the graphite crucible must be considered. The beneficial influence of a higher initial concentration of NaF activator strongly indicated that progressive activator loss from the pack did act to limit the quantity of vanadium transferred (viz, 3.4 mg/cm<sup>2</sup> at 1.0 percent NaF versus 5.2 mg/cm<sup>2</sup> at 3.3 percent NaF).

The vanadium coatings obtained by argon pack were not continuous and had a KHN of 300 ( 50 gm load) compared to the chromium with a KHN of 190. It was felt that some interstitial contamination had occurred and that softer coatings would be obtained if the impurity level (O<sub>2</sub>, N<sub>2</sub>) were further reduced. Since argon, with an estimated impurity level of 10 ppm contains about 100 times the concentration of interstitial impurities as a modest vacuum of  $1 \times 10^{-4}$ , it was decided to investigate a vacuum pack process for vanadium deposition.

## Vacuum Pack Process

Vacuum environment was expected to increase the vaporization rates of both activator and vanadium fluorides (also of chromium) by increasing the mean free paths. Vacuum environment was also expected to result in less contamination. Because of these factors, the vacuum pack process was explored for vanadium deposition resulting in a study of the various parameters; viz, temperature, time, activators, and different retort materials.

Experimental data accumulated during the investigation of the influence of these various parameters, resulted in progressive minor modifications of the experimental techniques. It is therefore desirable to give a brief description of the basic vacuum pack technique before discussing the various experimental procedures.

All of the initial exploratory runs were made in small cylindrical retorts, 3 inches long with an inside diameter of approximately 1.5 inches. The pack consisted of a mixture of vanadium granules (99.8 percent) and the fluoride activator, into which the specimens (arc-melted chromium buttons) were placed directly. Stainless steel, tantalum, and vanadium were used as retort materials and, except for the case where vanadium was used, the pack mixture and specimens were encapsulated in vanadium foil envelopes.

The packs were then sealed in the following manner:

A disc, having a small central hole, was TIG welded onto the open end of the cylinder. The pack was evacuated in the electron beam (EB) welder overnight (15 hours) under a dynamic vacuum of  $10^{-4}$  Torr. The small hole was then sealed by EB welding a small plug of metal (same material as the retort) over the hole.

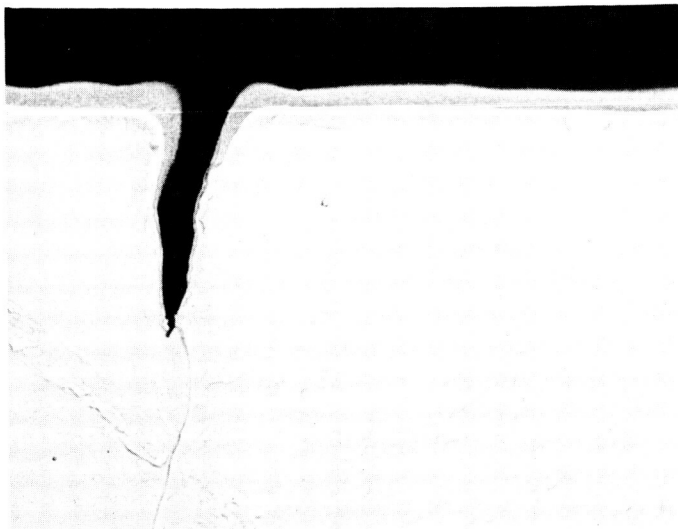
Subsequent firing was conducted in a large, cold-wall, vacuum furnace so that high vacuum conditions were obtained both inside and outside the retorts.

A temperature range of 2000 to 2400 F was investigated since this range includes the range ( $> 2200$  F) at which rapid interdiffusion of vanadium into chromium occurs, and the range ( $< 2200$  F) at which no significant weight loss in chromium occurs by vaporization. A series of 15-hour runs at 2000, 2100, 2150, 2200, 2300, and 2400 F were conducted and the results are summarized in Table VIII

TABLE VIII  
VANADIUM VACUUM PACK DATA

Process Temperature (F)	Process Time (hr)	Type Retort Material	Activator Level (%)	Change in Button Weight (mg/cm <sup>2</sup> )	Thickness of Vanadium Diffusion Layer (in.)
2000	15	321 Stainless Steel	1.0 NaF	(+)1.7	0.0001
2100	15	321 Stainless Steel	1.0 NaF	(+)3.2	0.0004
2100	75	321 Stainless Steel	1.0 NaF	(+)0.13	0.0004
2150	15	321 Stainless Steel	1.0 NaF	(+)0.63	0.0002 to 0.0004
2200	15	Tantalum	1.0 NaF	(+)2.2	0.0002 to 0.0003
2300	15	Tantalum	1.0 NaF	(+)4.3	0.001
2300	75	Tantalum	1.0 NaF	(-)78.2	---
2400	15	Tantalum	1.0 NaF	(-)76.6	---
	15	Tantalum	1.0 NaF	(+)7.5	0.0005 to 0.00075
2100	15	Tantalum	1.0 K <sub>2</sub> VF <sub>5</sub>	9.5	0.0005 to 0.00075
2100 (first run)	15	Tantalum	1/2% NaF + 1/2% K <sub>2</sub> VF <sub>5</sub>	7.0	0.00075 to 0.001
2100 (second run)	15	Vanadium	1/2% NaF + 1/2% K <sub>2</sub> VF <sub>5</sub>	22.0	0.00075 to 0.001
2100 (first run)	15	Vanadium	1/2% NaF + 1/2% K <sub>2</sub> VF <sub>5</sub>	15.7	0.001
All samples were arc-melted iodide chromium buttons.					

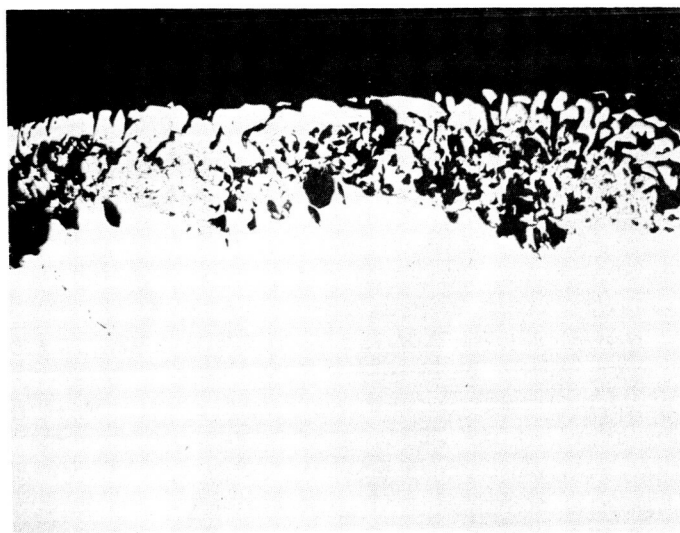
The data in Table VIII express the magnitude of the chromium evaporation problem, especially at 2300 F. (Even at 2200 F, the equilibrium vapor pressure of pure chromium is approximately 10,000 times greater than that of pure vanadium.) This situation possibly explains why even the presence of a high-vanadium coating upon the chromium specimens (2200 to 2400 F) apparently can do little to curb the powerful evaporation tendency of chromium. (This evaporation occurs in spite of the decreased activity of the chromium surface due to alloying.) For example, an interesting weight gain of (+)4.3 mg/cm<sup>2</sup> was recorded at 2300 F for a 15-hour run, but the net gain turned into a net loss of (-)78.2 mg/cm<sup>2</sup> after a prolonged run of 75 hours. Actually, the coating process is very probably reversed under certain conditions so that the vanadium in the pack may become progressively coated with chromium; and at some point the activity of surface vanadium becomes so low that the vanadium transfer



Magnification: 1000X

FIGURE 32.

GRAIN BOUNDARY VOID FORMATION  
IN CHROMIUM BUTTON DURING  
VANADIUM VACUUM PACK PROCESS;  
Coating Run at 2200 F



Magnification: 250X

FIGURE 33.

EXTENSIVE SURFACE VAPORIZATION  
IN CHROMIUM BUTTON DURING  
VANADIUM VACUUM PACK PROCESS;  
Coating Run at 2300 F

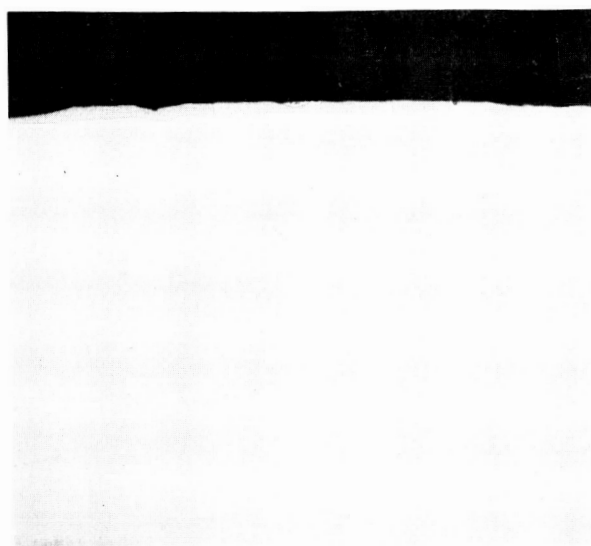


mechanism stops. Figures 32 and 33 are cross sections of buttons showing typical surface conditions after vacuum pack runs at 2200 and 2300 F using 1 percent NaF activator. The preferential grain boundary void formation (Fig. 32) which occurred at 2200 F was believed to be the beginning stage of corrosion or vaporization which becomes more severe at higher temperatures.

Uniform and smooth vanadium coatings (0.00075 inch thick) were obtained by runs of 2100 F for 15 hours using 1 percent NaF and 1 percent  $K_2VF_5$  activators in tantalum containers, but these coatings were quite hard (KHN of  $\sim 1100$ ).

Because the chromium buttons were not hardened appreciably, it was concluded that responsible contaminants were derived from absorbed films of  $O_2$  and/or  $N_2$  upon the fluoride activators or from water of hydration gradually accumulated by the same activators (released during pack processing). To rid the activators of potential contaminants, the fluoride salts were baked 2 hours at 450 F in a drying oven; then used to make vacuum packs identical to those which produced the hard coatings. This time, however, the packs in tantalum cannisters were first induction heated to 1600 F for 20 minutes in high vacuum to drive off all remaining sources of contamination. (Exit holes were drilled in the cannister tops.) After cooling to room temperature in vacuum, the tantalum cannisters were transferred immediately to an EB welder for sealing; the normal practice. Very encouraging results were obtained with these vacuum packs in simultaneous runs of 2100 F for 15 hours. Again, both activators produced vanadium coatings 0.00075 inch thick (weight increases of  $9.5 \text{ mg/cm}^2$  with  $K_2VF_5$  and  $7.5 \text{ mg/cm}^2$  with NaF). Of most importance, the coating hardnesses were markedly reduced to a KHN of 470/482 for the  $K_2VF_5$  pack and to a KHN of 355/383 for the NaF pack.

Fluoride activators with higher vapor pressures than NaF were then tried in an attempt to increase the vanadium fluoride concentration in the sealed packs. Potassium fluoride, with about 25 times the vapor pressure of NaF at 2100 F, was evaluated as an activator in Type 321 stainless steel cans, but it exhibited very low deposition rates and failed to produce continuous coatings in runs of 25 and 137 hours at 2100 F. This was attributed to the attack of KF on the stainless steel container. However, uniform 0.0003- to 0.00075-inch thick coatings were obtained using purified 1 percent NaF or 1 percent  $K_2VF_5$  as activator for runs of 15 hours at 2100 F.



Magnification: 100X



Magnification: 1000X

Thickness of Vanadium Coating is 0.0075 inch      Weight Gain = 7 mg/cm<sup>2</sup>

FIGURE 34. VANADIUM DEPOSITION BY VACUUM PACK PROCESS USING A MIXED FLUORIDE AS AN ACTIVATOR; 2100 F for 15 Hours in Tantalum Retort



KHN  
(50 gm load)

← 245

← 235

← 221

← 211

← 204

Magnification: 1000X

Thickness of Vanadium Coating is about 0.001 inch.      Weight Gain = 15 mg/cm<sup>2</sup>

FIGURE 35. VANADIUM DEPOSITION BY VACUUM PACK PROCESS USING A MIXED FLUORIDE AS AN ACTIVATOR; 2200 F for 15 Hours in Vanadium Retort

Better deposits were obtained using tantalum retorts, and similar thicknesses (0.0005 to 0.001 inch) of vanadium were obtained from packs containing 1 percent NaF, 1 percent  $K_2VF_5$ , and 0.5 percent NaF + 0.5 percent  $K_2VF_5$  after 15-hour runs at 2100 F. However, the softest (KHN of 200/235) and most uniform deposit in this series was produced by the mixed activator pack (Fig. 34).

The problem of producing a soft, ductile vanadium coating was effectively solved by using vacuum dried packs with a mixed fluoride salt activator. Generally, improved coatings were achieved by using tantalum retorts instead of stainless steel, and it was decided to further investigate the influence of retort materials on coating thickness.

The use of vanadium retorts with the mixed activator pack, resulted in a coating thickness of 0.001 inch for a run of 15 hours at 2200 F (weight gain  $15 \text{ mg/cm}^2$ ) with a hardness of 230 to 245 (Fig. 35). One specimen, from the earlier run (tantalum retort) with  $7.3 \text{ mg/cm}^2$  vanadium, was included in this pack and showed a total weight gain of  $22 \text{ mg/cm}^2$ , a net increase on the second run of  $14.7 \text{ mg/cm}^2$ . The total coating thickness on the sample was 0.00175 inch (Fig. 36).

#### Process Selection

The high-pressure argon pack process was thoroughly investigated and it was found that all attempts to reduce interstitial contaminant levels resulted in reduced deposition rates. Low deposition rates were attributed to the progressive loss of activator, but the addition of additional activator resulted in harder coatings and increased corrosion or vaporization of the chromium substrate. The highest deposition after a 15-hour cycle was about  $5.0 \text{ mg/cm}^2$  with a KHN of 300.

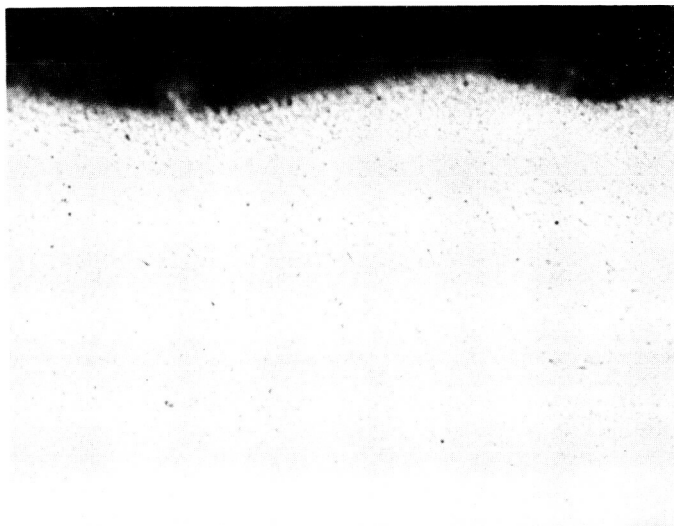
Development of the vacuum pack process for vanadium deposition yielded satisfactory coatings on pure chromium buttons, and preliminary experiments showed that a similar coating was obtained on Cr-5W alloy specimens. A smooth, uniform deposit of  $15.0 \text{ mg/cm}^2$  of vanadium (corresponding to about 0.001 inch) with a hardness of KHN 230 to 245 was achieved in a single 15-hour run at 2100 F.

Optimization of the process to achieve these results included selection and purification of activator, choice of retort material, and the investigation of process temperature.



Magnification: 100X

KHIN  
(50 gm load)



Thickness of Vanadium Deposit is 0.00175 inch.

Weight Gain = 22.0 mg/cm<sup>2</sup>

← 235

← 241

← 223

Magnification: 1000X

FIGURE 36. VANADIUM DEPOSITION BY VACUUM PACK PROCESS USING A MIXED FLUORIDE AS AN ACTIVATOR; 2200 F for 15 Hours and Two Cycles - First Cycle in Tantalum Retort, Second Cycle Vanadium Retort

It was concluded from these experiments that the upper limit of temperature for the operation of vacuum and high-pressure packs is about 2200 F. Surface instability of chromium, because of its increased vapor pressure and reactivity with molten activator, and the fact that free energies of formation of  $\text{VF}_2$  and  $\text{CrF}_2$  approach similar values (below 2200 F,  $\text{VF}_2$  becomes increasingly more stable than  $\text{CrF}_2$ ) make vanadium pack deposition appear impractical above 2200 F.

The vacuum pack process, using sealed vanadium retorts and a purified  $\text{NaF}$  and  $\text{K}_2\text{VF}_5$  mixed activator, was therefore selected as the most suitable technique to deposit vanadium.

#### Vanadium Coating of Program Specimens

The objectives of the program were to coat a large number of Cr-5W coupon specimens, 2 inches by 1 inch by 0.063 inch for subsequent oxidation testing at 1500, 2100, and 2400 F. These specimens were somewhat larger than the 1/2 inch by 3/4 inch sheet samples used in preliminary studies and larger retorts were required to carry out the vanadium deposition work.

Serious delays in the program were encountered due to the repeated postponements of the supply of vanadium sheet that were required for construction of the retorts. The order for the vanadium sheets was eventually cancelled by the suppliers owing to insurmountable problems associated with processing this material. The processing problems can probably be traced to the extreme difficulty of obtaining large ingots of vanadium containing less than the 1000 ppm  $\text{O}_2$  necessary to achieve good workability. No other commercial suppliers of vanadium could be found.

With the first postponement of the vanadium shipment, it was decided to investigate the use of large tantalum retorts since reasonably good vanadium coatings had been obtained with the small retorts in the initial experiments.

Two retorts, 5-1/4 inches in diameter by 5-1/2 inches high, were constructed from 0.065-inch tantalum sheet. One of the retorts was filled with vanadium granules and a 1 percent mixture of  $\text{NaF} + \text{K}_2\text{VF}_5$ , evacuated, and fired at 2600 F for 16 hours. It was hoped that plating the inside of the retort with vanadium would provide a similar environment for the chromium samples as a pure vanadium retort.

Following the previously described outgassing and evacuating techniques, this vanadium-plated, tantalum retort was loaded with 22 specimens having a 1/8-inch diameter hole at either end to facilitate subsequent titanium deposition by the fused

salt process and molybdenum deposition by vapor phase plating technique. The retort was then heated in a cold wall vacuum furnace for 15 hours at 2150 F.

After this run, it was observed that a crystalline, rough deposit was obtained on the samples. The deposit was most pronounced on one side of the samples (usually the side facing the retort walls) and on the bottom edge of the samples. Weight gains, after mechanically scraping the specimen surfaces to remove as much of the rough deposit as possible, were 14.2 to 16.8 mg/cm<sup>2</sup>.

It was thought that an excessive amount of activator produced localized liquid phase transport. On the second run, the activator concentration was reduced to 0.1 percent NaF + 0.25 percent K<sub>2</sub>VF<sub>5</sub> and the halide salts were mixed with a small amount of vanadium granules and placed on the bottom of the pack to prevent direct contact with the specimen. An additional 12 specimens, having about 11 mg/cm<sup>2</sup> vanadium deposit from an earlier run, were included in this pack.

Again, after 15 hours at 2150 F a rough crystalline growth was obtained, with preferential deposition on one side and along the bottom edge of the specimens. Weight gains after this run were 11.3 to 15.2 mg/cm<sup>2</sup>.

A third run was made using a very small amount of activator (0.01 percent) in an attempt to corrode away the rough, high surface area of crystalline deposits, but only resulted in some sintering of fine particles from the pack. A gradual deterioration of the vanadium granules by the growth of small crystals and subsequent disintegration of coarse granules resulted during these experiments.

With the receipt of a new batch of vanadium granules it was decided to run a series of experimental retorts simultaneously in an attempt to find a solution and to allow satisfactory vanadium deposition from tantalum retorts. The type of retort, pack compositions, and subsequent observations after deposition cycles of 15 hours at 2150 F are listed in Table IX.

TABLE IX  
SUMMARY OF RETORT RUNS TO OBSERVE PROCESS VARIABLES

PACK NUMBER	1	2	3	4	5	6
RETORT MATERIAL	Tantalum	Tantalum	Tantalum with Tungsten lining	Tantalum	Tantalum	Vanadium
RETORT SIZE (Diameter in inches)	5-1/4	1-1/4	1-1/4	1-1/4	1-1/4	3
VANADIUM GRANULE SIZE	+20 Mesh	+20	+20	+20	-100	+20
ACTIVATOR	0.1% (NaF + K <sub>2</sub> VF <sub>5</sub> )	1.0% (NaF + K <sub>2</sub> VF <sub>5</sub> )	0.1% (NaF + K <sub>2</sub> VF <sub>5</sub> )	1.0% (NaF + K <sub>2</sub> VF <sub>5</sub> )	0.1% (NaF + K <sub>2</sub> VF <sub>5</sub> )	1.0% (NaF + K <sub>2</sub> VF <sub>5</sub> )
ATMOSPHERE INSIDE RETORT	Vacuum (10 <sup>-5</sup> )	Vacuum	Vacuum	Argon (1 atm)	Vacuum	Vacuum
OBSERVATIONS	Pack sintered. Considerable crystal growth on vanadium granules and specimens. Granules discolored.	Some pack sintering. Granules discolored. No noticeable crystalline growth on granules. Slight crystalline deposit on specimens.	No pack sintering. Vanadium granules colored gold. Specimens gold/brown.	No pack sintering. Granules clean. Specimens very clean.	Pack sintered solid.	No pack sintering. Granules very clean. Specimens very clean. One or two sintered particles.
	Weight gains - Specimens in pack = 18.7 mg/cm <sup>2</sup> . Specimens suspended above pack = 11.3 mg/cm <sup>2</sup>	Weight gain = 5.61 mg/cm <sup>2</sup>	Weight gain = 0.89 mg/cm <sup>2</sup>	Weight gain = 3.2 mg/cm <sup>2</sup>	No recorded weight gains.	Weight gain = 6.89 mg/cm <sup>2</sup>

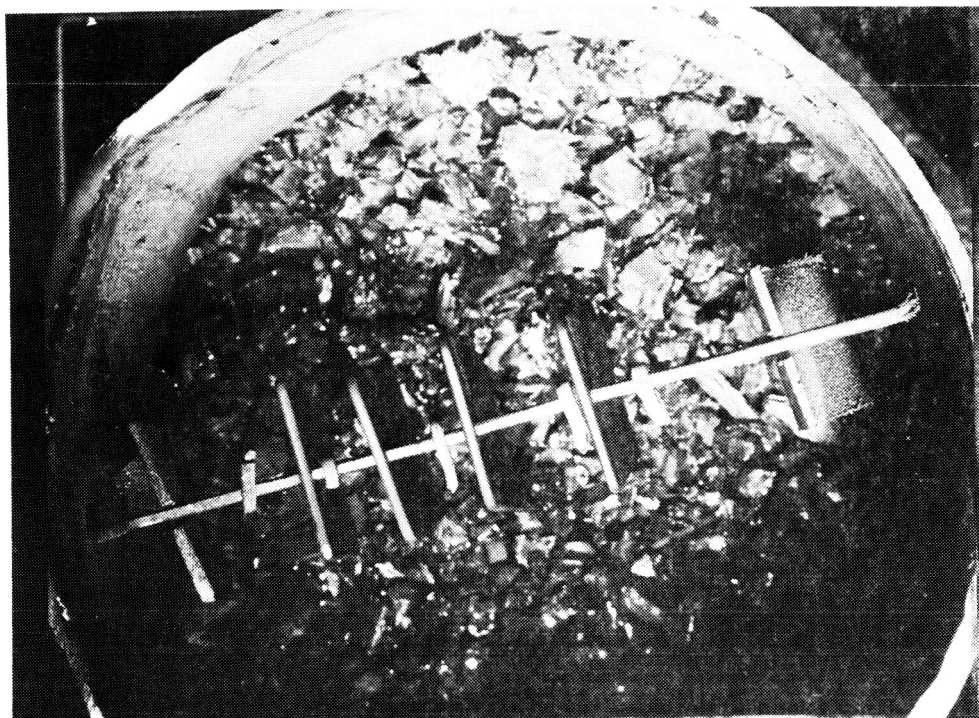


FIGURE 37. TANTALUM RETORT AFTER 15 HOURS AT 2150 F; Specimens Suspended Above Pack

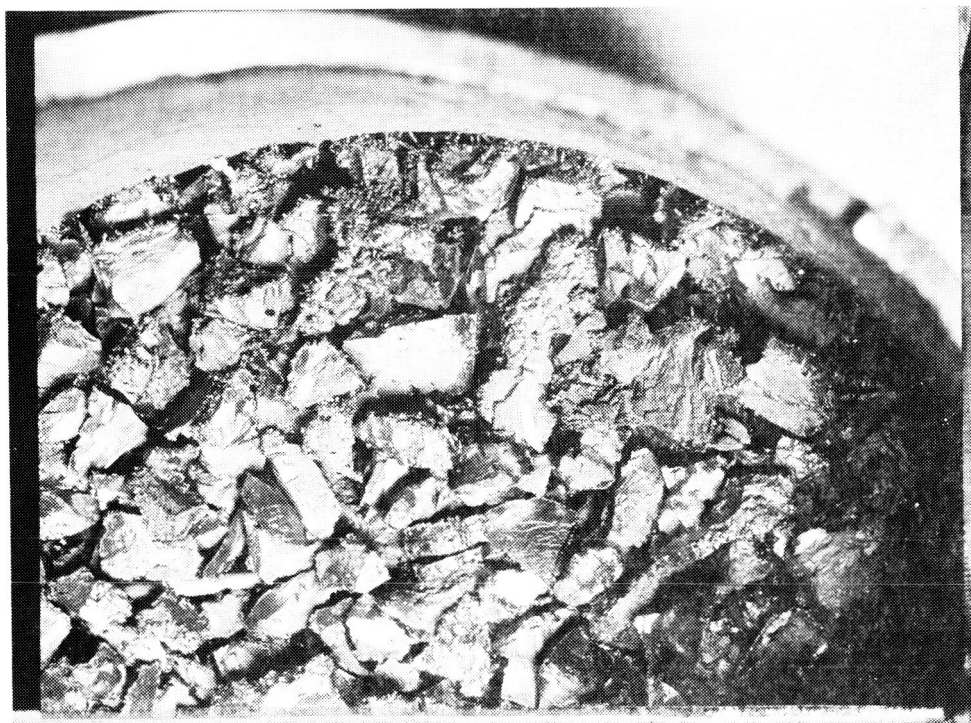


FIGURE 38. TANTALUM RETORT AFTER 15 HOURS AT 2150 F; Crystalline Growth on Vanadium Granules



Pack Number 1 contained four specimens buried in the pack in the usual manner, and four specimens suspended above the pack on a tantalum wire supported by a tantalum strip support. A considerable amount of crystalline growth occurred on the vanadium granules with a strongly preferred growth direction towards the retort walls. The appearance of the pack upon opening this retort is shown in Figures 37 and 38.

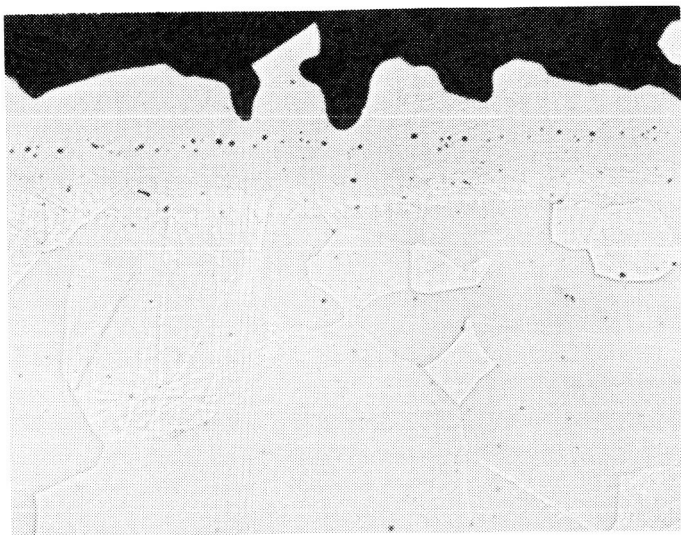
A considerable amount of crystalline deposition occurred on specimens within the pack, while a generally smoother coating was obtained on samples suspended above the pack. However, there was a variation in the surface appearance of these latter specimens over their entire length; the specimens being bright, with some crystalline deposition at the bottom (closest to the pack), and having a grey matte appearance towards the top. Metallography showed a fairly uniform thickness of coating. The coating at the bottom end of the specimens had a KHN of about 330, the coating at the top of the specimens was extremely brittle, with a KHN of about 1100. Cracking of the coating in this area made accurate hardness determinations difficult.

It was observed that the tantalum retort was being corroded away during the coating process at the rate of about 0.003 inch/15 hours, and it was suspected that tantalum was depositing both on the samples and granules. The free energies of formation of vanadium, chromium, and tantalum fluorides are sufficiently close ( $-\Delta F^\circ$  values for  $MF_2$  at 1400 K being 76, 69, and 70, respectively) to make this a reasonable transport mechanism, in addition to any unexplained electrochemical effects.

Dissolution of vanadium granules in  $HNO_3$  left a thin shell of metal which was not soluble in HCl, but was soluble in  $HF/HNO_3$  solution, indicating tantalum or tantalum-rich metal. Qualitative spectrographic analysis using new granules as a standard showed that the vanadium granules after a coating run contained slightly more tantalum, while the undissolved residue was primarily tantalum with only a slight increase in chromium content.

X-ray fluorescent analysis of one of the Cr-W specimens suspended above the pack was carried out. These results are:

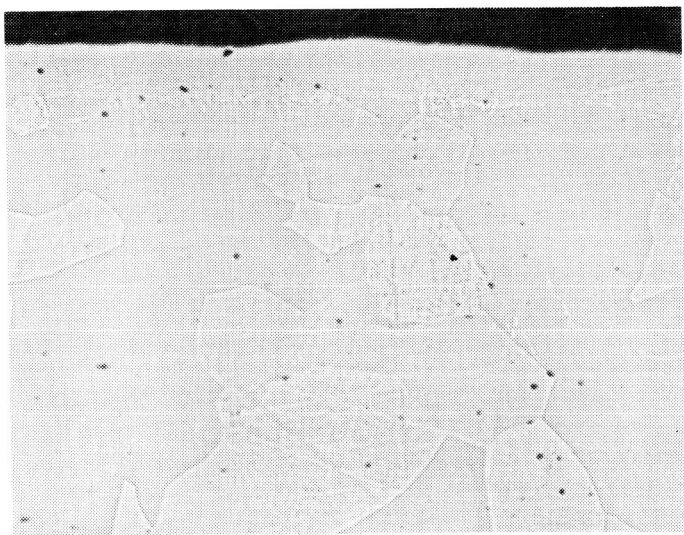
Metal	Standard (uncoated specimen)	Coated Specimen		
		Top	Middle	Bottom
Vanadium	23.8 counts/sec	264.9	338.3	492.3
Chromium	7062.1	897.6	408.7	259.1
Tantalum	68.4	4224.4	3926.4	3468.8
Tungsten	1818.2	1984.5	1839.1	1775.3



Magnification: 100X

**FIGURE 39.**

**VANADIUM DEPOSITED ON Cr-5W  
IN TANTALUM RETORT; Surface  
Facing Retort Wall**



Magnification: 100X

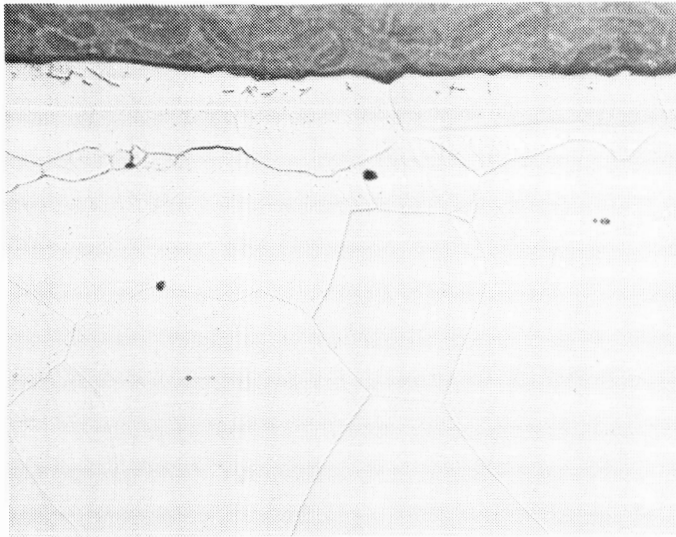
**FIGURE 40.**

**VANADIUM DEPOSITED ON Cr-5W  
IN TANTALUM RETORT; Surface  
Facing Center of Pack**

These data show conclusively that tantalum was being deposited on both the chromium samples and vanadium granules. The strongly directional crystalline or dendritic vanadium/tantalum deposit (Fig. 39 and 40) was very similar in appearance to the type of plate obtained from an electrolytic bath when too high a current density is used. A possible explanation is that temperature gradients across the large pack were causing concentration cells, which, in turn, resulted in accelerated, nonuniform deposition. Because of the unavailability of vanadium sheet, it was not possible to determine if the same problems would have been encountered with larger (hence heating and cooling temperature gradients) vanadium retorts. However, with the smaller packs (1-1/4- to 3-inch diameter) vanadium retorts yielded consistently smoother coatings with none of the potential problems of tantalum codeposition. Other retort materials which were studied included columbium and titanium. Both of these retort materials resulted in very unsatisfactory coatings, however.

To investigate the potential of the vanadium sink coating, the only recourse was to use small 1/2-inch by 1-inch specimens so that two experimental vanadium retorts (3-inch diameter by 3-inch high) could be used to coat a limited number of specimens. Both of these retorts had been used a number of times previously and had, therefore, been corroded away partially during processing runs. Leaks were generally found to occur in the retort lids after one or two processing cycles, but it was possible to obtain a sufficient quantity of vanadium foil (0.010-inch by 2-inch) to serve as welding filler material.

Forty specimens, with radiused edges and end holes to facilitate titanium and molybdenum deposition, were loaded into these retorts and coated with 8 to 10 mg/cm<sup>2</sup> vanadium in two, 15-hour runs at 2150 F using 0.1 percent activator initially separated at the bottom of the pack. On a third coating run, both retorts developed cracks and holes down the sides, making repair impossible. The escape of fluoride vapors into the vacuum chamber made mass transport to specimens negligible. The appearance of the resulting coating is shown in Figure 41. With no currently operable processes for further vanadium deposition, it was decided to use these specimens to investigate systems C1 through C5.



Magnification: 500X

FIGURE 41.  
VANADIUM DEPOSITED ON Cr-5W  
BY VACUUM PACK PROCESS;  
Vanadium Retort

#### Potential of Developing Vanadium Coatings

The potential of producing satisfactory deposits from fused salt by either electrolytic or electroless plating does exist. Tests have revealed that vanadium of satisfactory purity may be deposited, but the very serious problems of obtaining a smooth and uniform coating remain.

When the deposition rates from the fused salt are sufficiently high to be practical, the vanadium coating is nodular. Development of a fused salt deposition process for vanadium will require considerably more experimental work in order to optimize this process.

Although it cannot be stated absolutely that satisfactory deposits could be produced by pack cementation in large vanadium packs, it has been shown that acceptable coatings were obtained in 1-1/4-inch and 3-inch diameter retorts. These deposits in different runs varied from 6 to 12 mg/cm<sup>2</sup>. The deposits were generally smooth and uniform but had sinter sites (sintered vanadium particles) on the surface. These sintered particles were either retained as nodules on the coating or, upon removal, left pits in the coating. The concentration and severity of the sinter sites varied with granule size and coating thickness. The smaller the vanadium granules in the pack, the more frequent the sinter sites on the specimens; the thicker the deposit, the more severe the sintering.

Experiments utilizing tantalum retorts resulted in codeposition of tantalum and vanadium. In packs depositing as little as  $6 \text{ mg/cm}^2$ , the initiation of dendritic deposition was observed and chemical analysis proved the deposit to be a mixture of vanadium and tantalum. The other materials tested for retort construction gave similar results as shown in Table IX.

#### 4.2.3 Titanium Deposition

##### Pack Deposition

The vacuum pack deposition of titanium was tested on vanadized Cr-5W alloy specimens. Cylindrical retorts were prepared from titanium sheet. These packs were filled with a titanizing mixture that had been used successfully on other alloy work at Solar (AF33(615)-1259). The pack contents were 33W-67Ti alloy (-50 + 100 mesh) with 0.1 to 1.0 percent NaF as activator. The runs were conducted for the various times and temperatures listed in Table X.

TABLE X  
VACUUM PACK TITANIUM DEPOSITION

Temperature (F)	Activator	Time (hr)	Weight Gain ( $\text{mg/cm}^2$ )	Observations
2150	0.25% NaF	15	---	Very heavy sintering. No meaningful weight measurements.
2000	0.25% NaF	15	39 to 47	Much sintering.
2000	0.1% NaF	6	8.6 to 8.9	Some sintering.
1900	0.25% NaF	15	13.0	Some sintering.

Considerable sintering of titanium granules to the surface of the specimens was noted after each run, but was least severe after the 1900 F run.

The presence of even minor amounts of sintered particles on the surface are very undesirable since they give rise to localized variations in coating thickness. These variations result in physical and chemical inhomogeneity of the coating.

## Fused Salt Deposition

Titanium deposition is currently being investigated under contract AF33(615)-3173. Based on this contract effort, the following bath and process parameters were selected for study:

- |                           |   |
|---------------------------|---|
| • Bath composition (mol%) | 60LiF-40NaF - 95 percent (solvent)<br>K <sub>2</sub> TiF <sub>6</sub> - 5 percent (active salt)<br>Titanium (granules) - 50 percent of titanium<br>content in active salt |
| • Bath temperature        | 2000 F  |
| • Anode                   | Titanium welded cylinder of (99.7 percent)<br>sheet   |
| • Process                 | Nonelectrolytic   |

The rate of deposition on either Cr-5W alloy or vanadium-coated Cr-5W alloy was approximately 0.5 mil per hour.

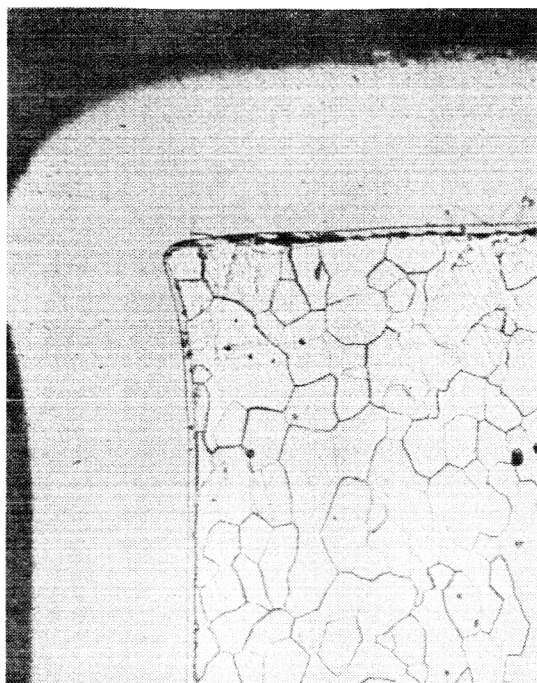
The specimens coated in the titanium fluoride bath appeared smooth, uniform, and lustrous when removed from the bath (Fig. 42). The coating is particularly outstanding over sharp edges. The diffusion layer at the interface is TiCr<sub>2</sub> Laves phase with a KHN of 1400.

## Titanium Process Selection

The vacuum pack deposition of titanium was successfully achieved; however, the process is restricted by severe sintering of titanium metal granules at temperatures greater than 1900 F. Any sinter sites in the coating are a serious liability to the resultant coating. Nonelectrolytic deposition in a fused salt bath is the preferred process for titanium deposition. The nonelectrolytic deposition process has excellent throwing power and can produce smooth coatings at a rapid deposition rate (0.001 inch in 2 to 3 hours at 2000 F).

### 4.2.4 Deposition of Molybdenum

Molybdenum (1 to 2 mils) was required for two of the proposed coating systems (V-Mo-Si and V-Ti-Mo-Si). Senderoff and Brenner (Ref. 17) described the production of dense coherent molybdenum by electrolysis from an all-chloride bath. Meredith and Campbell (Ref. 18) reported the investigation of electrodeposition of molybdenum from organic solvents. However, the most advanced method for the deposition of molybdenum coatings is chemical vapor deposition.



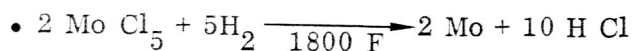
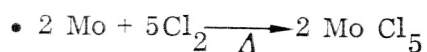
Magnification: 250X

FIGURE 42.  
TITANIUM DEPOSITED ON Cr-5W  
IN FLUORIDE BATH; 4 Hours at  
2000 F, Nonelectrolytic Process

### Application Technique

The San Fernando Laboratories (SFL) was subcontracted for chemical vapor deposition of molybdenum.

A typical reaction for the chemical vapor deposition of molybdenum is:



The actual reaction involves a mixture of molybdenum chlorides whose composition may be varied by varying the temperature of the molybdenum in the chloride generator. The molybdenum is deposited on a heated metal specimen by passing hydrogen and molybdenum chloride over the sample. The gases react on the heated metal surface to deposit molybdenum metal and liberate hydrogen chloride. The deposit has a typical columnar grain structure.

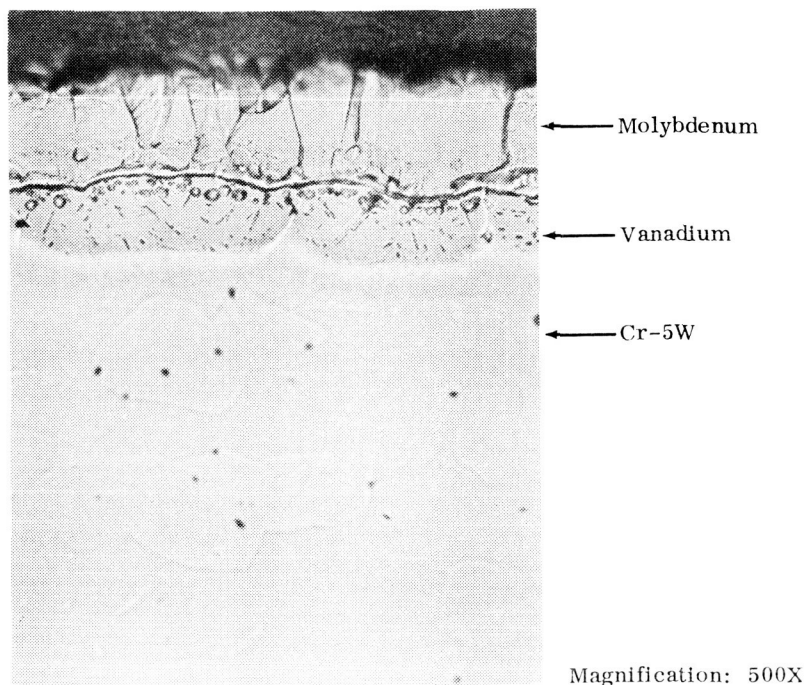


FIGURE 43. MOLYBDENUM DEPOSITED BY CHEMICAL VAPOR DEPOSITION

#### Coating of Program Specimens

Twenty Cr-5W samples (0.060 inch by 0.500 inch by 1.00 inch) were coated with pack-V or pack-V-fused salt-Ti and submitted to SFL for a 0.001- to 0.002-inch coating of molybdenum. All specimens were prepared with two holes to permit their support from wire hooks for the coating processes. To deposit molybdenum, a wire was hooked through a hole and the specimen was suspended in the reaction chamber. The chamber was designed to permit the addition of hydrogen through one tube and molybdenum chloride through another. The chloride was generated by passing  $\text{Cl}_2$  over heated molybdenum chips. These gases were mixed together and flowed over the sample during evacuation of the system. The sample was inductively heated by an external coil. The coatings deposited varied from 0.001 to 0.002 inch in four minutes. These coatings were acceptably smooth and uniform as shown in Figure 43.



## Discussion

The deposition of molybdenum by chemical vapor deposition was rapid (1 mil/3 to 5 minutes) and satisfactorily uniform. The total processing conditions are not available as they are SFL proprietary information. Two major restrictions imposed by this deposition technique are that samples must be uniformly heated by induction and exposed to the reaction gases. These two restrictions presented no serious problem for the preparation of small test specimens but would present a serious problem in coating large turbine parts or complex shapes.

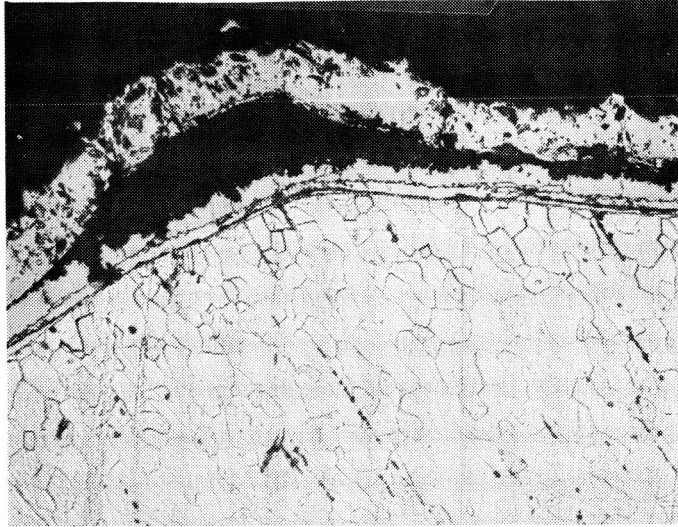
### 4.2.5 Deposition of Silicon

Based on related programs at Solar, the deposition of silicon from argon high-pressure packs was well understood. It was necessary to determine pack conditions and times to produce the most desirable coating for each of the several systems.

#### Deposition of Silicon on Cr-5W

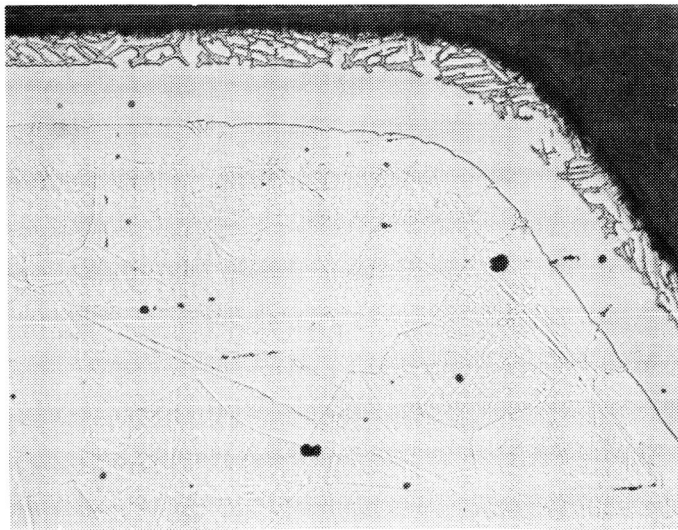
Initially, one sample of the chromium alloy was placed in a pack (-200 mesh Si + 1 percent NaF) with a series of columbium alloys and run for 4.5 hours at 1950 F. Whereas, the columbium alloys gained the expected 11 to 12 mg/cm<sup>2</sup>, the chromium sample gained 84 mg/cm<sup>2</sup> corresponding to about 0.012-inch coating of CrSi<sub>2</sub>. Packs were subsequently run at 1800 F for 2.5 and 1.75 hours resulting in 34 and 24 mg/cm<sup>2</sup>, respectively. Some edge spalling and "rabbit earing" was observed with these samples, but this problem was less severe with the thinner coating. One pack run was made at 2150 F for four hours with no activator, and again resulted in an excessively heavy coating (75.3 mg/cm<sup>2</sup>); however, no signs of edge cracking or spalling were present.

Although the 2150 F run apparently resulted in a better edge appearance, metallographic examination of all of the samples showed that this temperature produced the most porous coating and that the corner cracks observed with the low temperature runs did not extend through to the metal surface. On the basis of these observations, a temperature of 1800 F with a 1 percent NaF activated pack was selected to produce the desired coating (12 to 14 mg/cm<sup>2</sup>) on Cr-5W. Time required varied with retort size from one to three hours.



Magnification: 250X

**FIGURE 44.**  
**SILICIDED, TITANIUM-COATED**  
**Cr-5W ALLOY**



Magnification: 250X

**FIGURE 45.**  
**TITANIUM-COATED Cr-5W**  
**ALLOY; Diffused 4 Hours at**  
**2400 F In Argon**

### Deposition of Silicon on (Cr-5W)-V

The evaluation of the rate of deposition on vanadized Cr-5W was conducted along the same lines as that for Cr-5W. The deposition was found to be significantly lower than over the unalloyed material. It was subsequently determined that a temperature of 2150 F for two hours with pack composition (99.9 percent purity Si, -200 mesh + 1 percent NaF) would produce the desired weight gain of 12 to 14 mg/cm<sup>2</sup> (corresponding to 0.002-inch silicon).

The samples, when tested, indicated that heavier siliciding was desirable. Four hours at 2150 F produced a coating of greater than 20 mg/cm<sup>2</sup>. The rate of silicon deposition is inversely related to the vanadium thickness and as the vanadium decreases in thickness, the deposition rate approaches that obtained on unmodified chromium alloy.

### Deposition of Silicon on Cr-Ti or Cr-V-Ti

The titanized samples were tested to determine their siliciding rate. Samples were coated in a (-200 mesh silicon, 0.1 percent NaF activator) pack at 1900, 2000, and 2150 F.

When titanium is directly silicided, it crinkles due to coating growth stress as shown in Figure 44. To prevent this effect, the titanium was diffused for four hours at 2400 F to produce the structure shown in Figure 45. This diffused coating may be silicided with no detrimental coating growth. A similar anneal of the Cr-V-Ti sample resulted in metal diffusion without producing the Laves phase noted in Figure 45.

The annealed samples were then silicided and a layer of 12 to 14 mg/cm<sup>2</sup> was deposited in four hours at 2000 F. Corrosion tests revealed the need for heavier siliciding in which case an additional 12 to 14 mg/cm<sup>2</sup> was deposited in pack in four hours at 2150 F.

### Deposition of Silicon on Cr-V-Mo and Cr-V-Ti-Mo

The siliciding of molybdenum-coated samples was effected with a pack only slightly modified from the one made for Cr-V-Ti. The -200 mesh silicon plus 0.5 percent NaF activated pack at 2000 F required six hours to deposit 12 to 14 mg/cm<sup>2</sup>. An additional four hours at 2150 F added 8 to 10 mg/cm<sup>2</sup> to the previously deposited coating. The samples thus coated had a smooth uniform appearance.

# 5

## OXIDATION TESTING

### 5.1 EQUIPMENT, PROCEDURES, AND TEST SPECIMENS

All oxidation testing was performed in a static air environment in electrically resistance heated furnaces that utilized silicon carbide elements. During testing at 1500, 2100, and 2400 F, two-hour cycles were used for the first 100 hours and 20-hour cycles until failure or 500 hours accumulated exposure. Because of problems encountered in deposition of vanadium, oxidation testing was restricted to 2400 F for the V-Ti-Mo-Si coatings. Toward the end of the program, the 20-hour cycles were extended for some samples to last over a whole weekend to accumulate sufficient exposure time. Specimens were withdrawn for metallographic and chemical analysis after 100 hours (or failure), and after the maximum time tested.

Oxidation testing at 2400 F presents a number of problems in terms of supporting test specimens without causing premature rupture of the coating by high-pressure points of contact or by having a chemical reaction take place between the coating and support media. The most satisfactory support media was found to be a low density silica fiber material known as Dyna-Quartz. This material is available in sheet form and can be readily cut, but after firing becomes very fragile. Grooves were cut into 0.5-inch thick Dyna-Quartz and the specimens were supported so that the whole of one surface and all of the edges were freely exposed to the atmosphere. This Dyna-Quartz tray was then supported on pre-fired alumina brick.

It was generally found that Dyna-Quartz was completely inert to silicide coatings unless the coating was of a composition that produced a low melting point glass.

The original program requirements were for cyclic oxidation tests to be conducted on Cr-5W sheet specimens 1 inch by 2 inches by 0.063 inch so that valid reliability data could be obtained. But, because of the problems encountered in the deposition of vanadium, it became necessary to coat smaller samples (1/2 inch by 3/4 inch by 0.063 inch) to obtain oxidation data on the vanadium-base coatings.

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TABLE XI

SUMMARY OF WEIGHT CHANGE DATA AND VACUUM FUSION ANALYSIS IN  
OXIDIZED Cr-5W AND (Cr-5W)-Si

Specimen	Exposure Temperature (F)	Exposure Time (hr)	Total Weight Change (mg/cm <sup>2</sup> )	Vacuum Fusion Analysis <sup>(1)</sup>		Micro-Kjeldhal N <sub>2</sub> (wt %)
				O <sub>2</sub> (wt %)	N <sub>2</sub> (wt %)	
Cr-5W	As-received	As-received	--	0.15 <sup>(5)</sup>	0.0021 to 0.0023 <sup>(5)</sup>	--
Cr-5W	1500	500	+ 0.2 to 0.7	0.10 <sup>(5)</sup>	0.078 <sup>(5)</sup>	--
(Cr-5W)-Si	1500	500	1.1 to 1.2	0.007 to 0.01 <sup>(3)</sup>	ND <sup>(2)</sup> (3)	--
Cr-5W	2100	500	8.2 to 10.3	0.40 <sup>(5)</sup>	0.67 <sup>(5)</sup>	--
(Cr-5W)-Si	2100	500	(-) 1.5 to (+) 1.8	0.008 to 0.01 <sup>(3)</sup>	0.0064 to 0.007 <sup>(3)</sup>	--
(Cr-5W)-Si	2100	500	- 1.5 to + 1.8	0.15 <sup>(4)</sup>	0.11 to 0.17 <sup>(4)</sup>	--
Cr-5W	2400	90	(-) 34 to (-) 38	0.074 <sup>(5)</sup>	2.75 <sup>(5)</sup>	2.1
(Cr-5W)-Si	2400	120	(-) 16 to (-) 18	0.049 <sup>(3)</sup>	0.012 <sup>(3)</sup>	--

- Analyses conducted after removal of oxide scale or silicide.
- ND = Not detectable.
- Coating removed by surface grinding.
- Sample analyzed with coating retained on surface.
- Electro-etched.

Specimens were cut to the desired sizes on an electrobandsaw. Specimens which were to be subsequently coated with titanium or molybdenum were drilled, using a carbide drill, to produce 1/8-inch diameter holes. All edges were radiused by hand-grinding and the specimens were cleaned by electropolishing and degreasing. Table XI summarized the deposition weight of the coating subjected to testing.

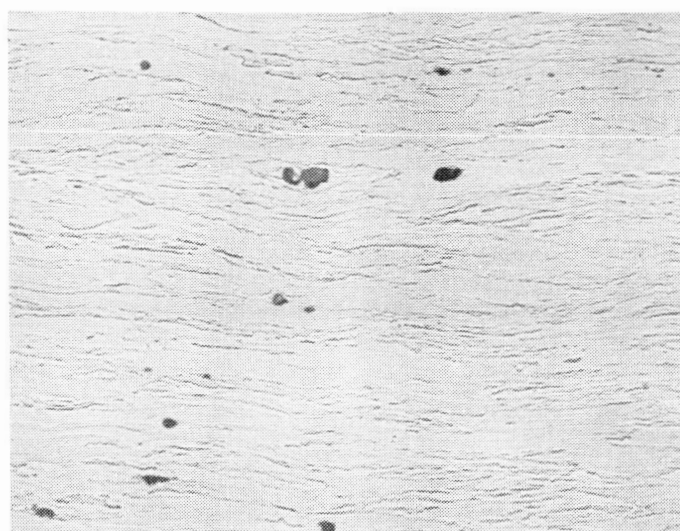
## 5.2 OXIDATION TEST RESULTS

### 5.2.1 Oxidation Testing of Cr-5W and (Cr-5W)-Si

Full-size specimens (1 inch by 2 inches by 0.063 inch) of uncoated chromium alloy and samples coated with the unmodified chromium silicide were tested at 1500, 2100, and 2400 F to provide base-line oxidation data. Surprisingly good protection was afforded by the unmodified silicide coating at 2100 F and the spalling rate at 2400 F was moderate.

The alloy in the as-received condition has a cold worked structure (KHN of 295 to 351) with oxide particles randomly dispersed throughout the matrix (Fig. 46). Siliciding at 1800 F for 2-1/3 hours, which deposited  $14.0 \text{ mg/cm}^2$ , was sufficient to cause partial recrystallization of the chromium alloy (Fig. 47). It was observed during the initial deposition studies that silicon diffuses into chromium extremely rapidly, and that three silicides of chromium are formed during high temperature exposure ( $> 1800 \text{ F}$ ). The literature reports the existence of seven silicides of chromium, but it is probable that only  $\text{Cr}_3\text{Si}$ ,  $\text{Cr}_5\text{Si}_3$ ,  $\text{CrSi}$ , and  $\text{CrSi}_2$  exist. These have, respectively, cubic, tetragonal, cubic, and hexagonal structures. From metallographic observations and by analogy with other known silicides, it is likely that the three silicide phases observed in these experiments are  $\text{CrSi}_2$ ,  $\text{CrSi}$ , and  $\text{Cr}_5\text{Si}_3$ , but they have not been positively identified.

Thermogravimetric data for static air exposure at 1500, 2100, and 2400 F of uncoated Cr-5W and (Cr-5W)-Si are given in Figures 48 through 53. Two-hour cycles were used for the first 100 hours, followed by 20-hour cycles up to 500 hours exposure, and five specimens were exposed for each test. In general, the weight change curves were virtually identical for each specimen in a particular group. However, Specimens No. 2 and 3 in the (Cr-5W)-Si group tested at 1500 F (Fig. 49) exhibited anomalous weight change at 50 hours which suggested spalling away of the coating followed by a temporary accelerated oxidation rate. Both samples were removed for examination but no obvious effects were detected. It should be noted that different scales are used

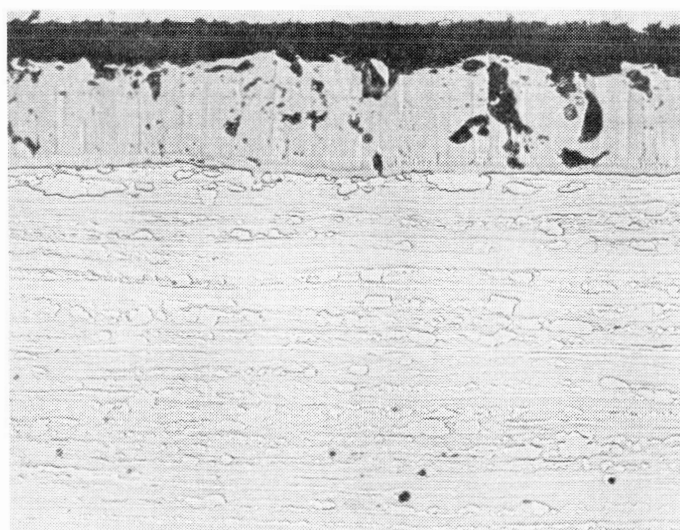


KHN  
(50 gm load)

← 295-351

Magnification: 500X

FIGURE 46.  
Cr-5W ALLOY, AS RECEIVED



KHN  
(50 gm load)

← 1565 Cr Si<sub>2</sub>

← 1000 Cr Si<sub>2</sub>

← 306 Cr

← 280

← 322

← 300

← 309

Magnification: 250X

FIGURE 47. Cr-5W ALLOY, PACK SILICIDED AT 1800 F 2-1/3 HOURS

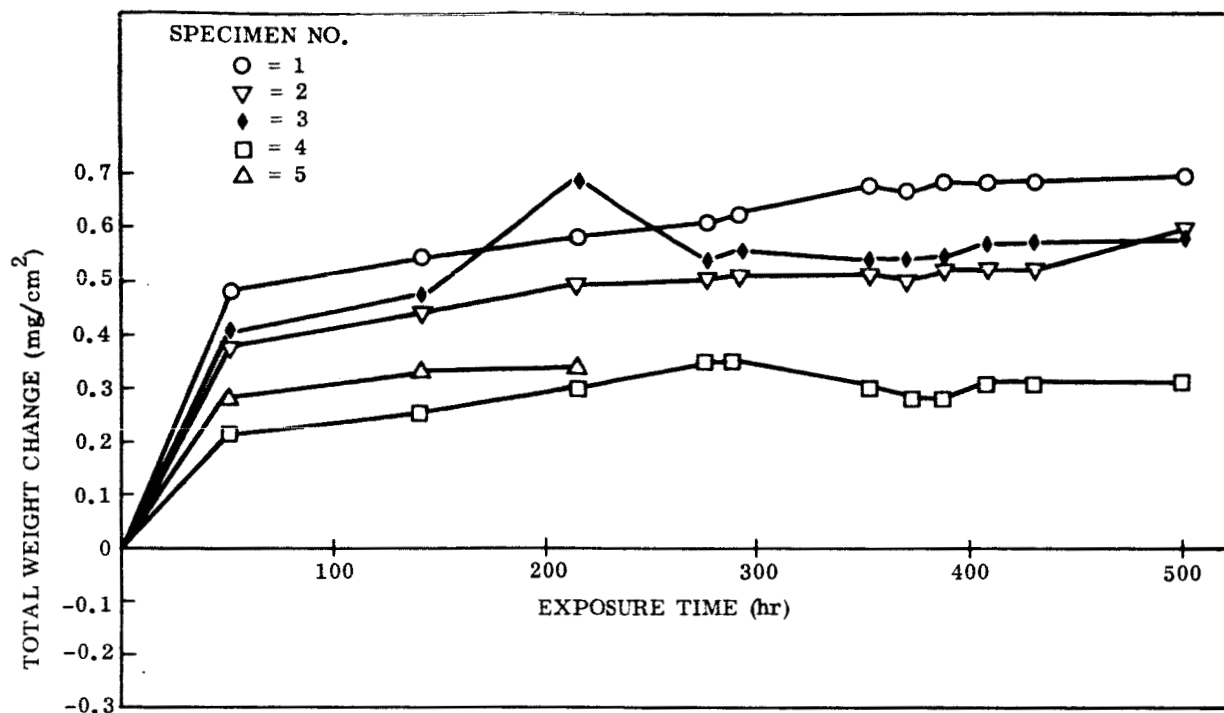


FIGURE 48. OXIDATION DATA FOR UNCOATED Cr-5W ALLOY; 1500 F

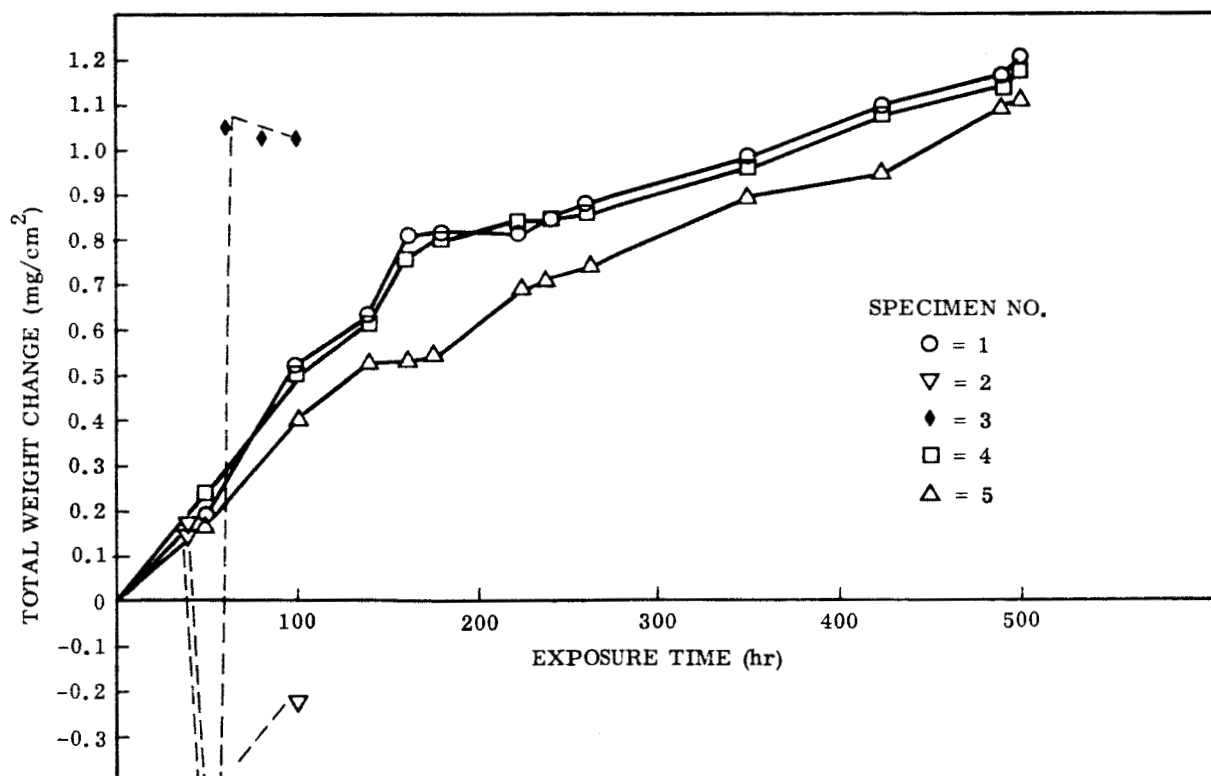


FIGURE 49. OXIDATION DATA FOR (Cr-5W)-Si; 1500 F



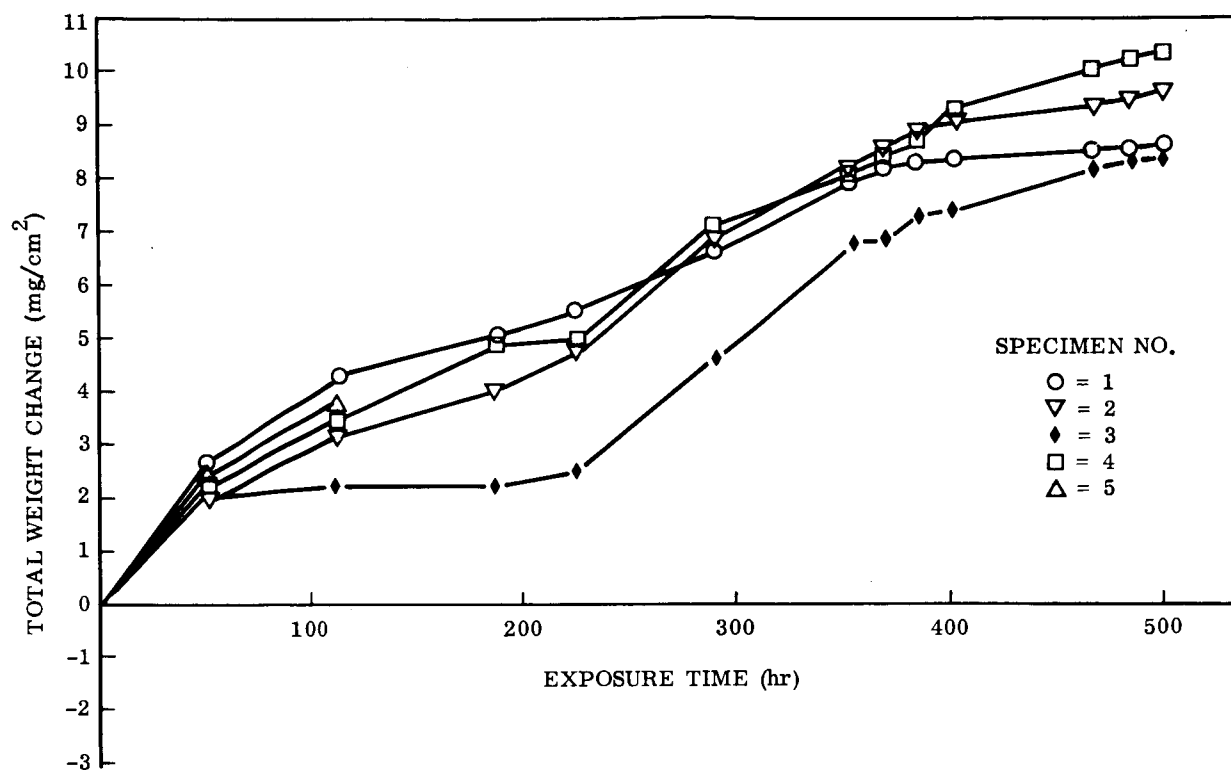


FIGURE 50. OXIDATION DATA FOR UNCOATED Cr-5W ALLOY; 2100 F

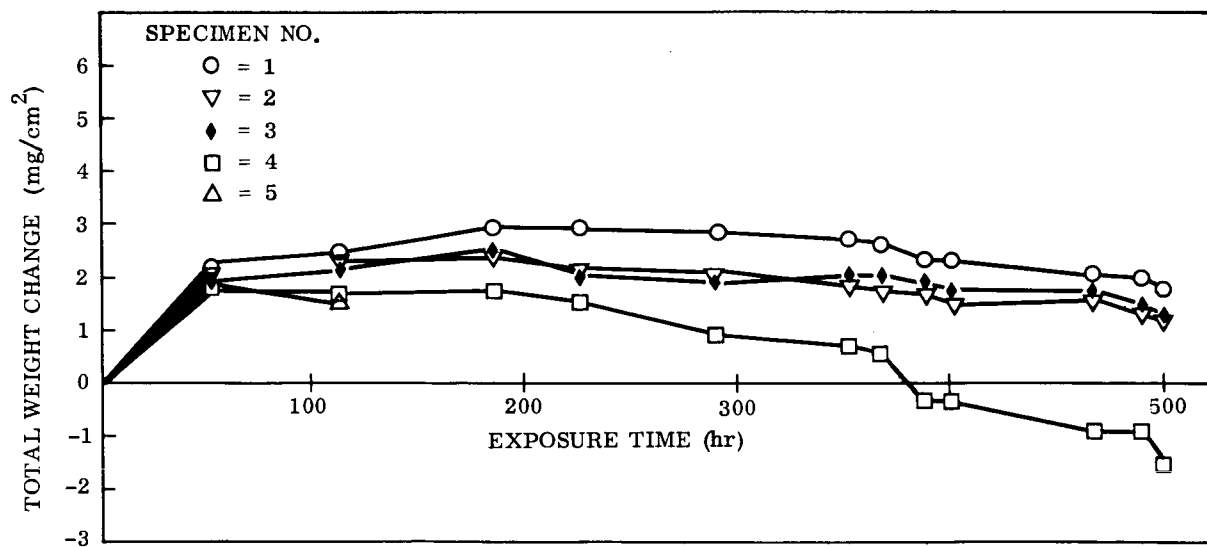


FIGURE 51. OXIDATION DATA FOR (Cr-5W)-Si; 2100 F

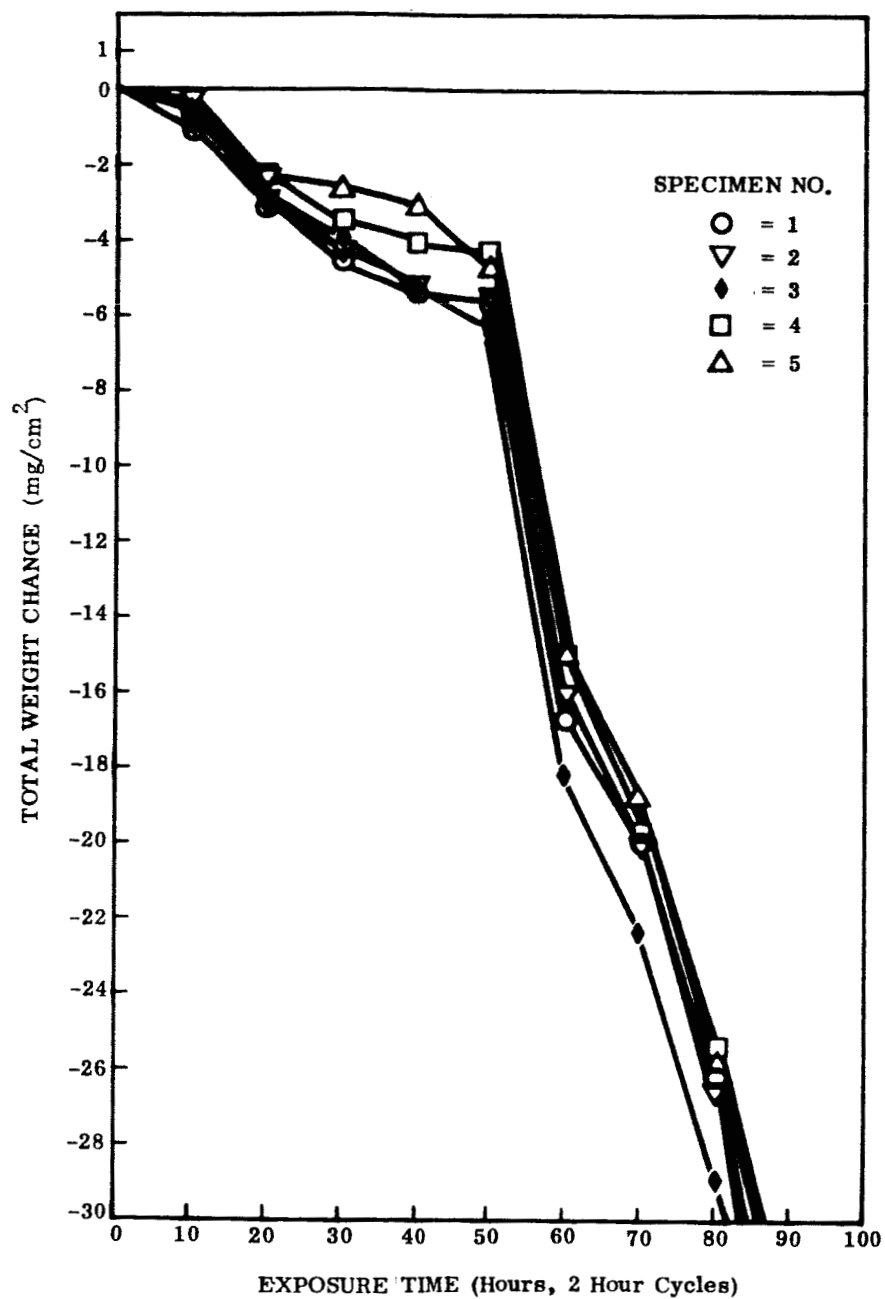


FIGURE 52. OXIDATION DATA FOR UNCOATED Cr-5W ALLOY; 2400 F

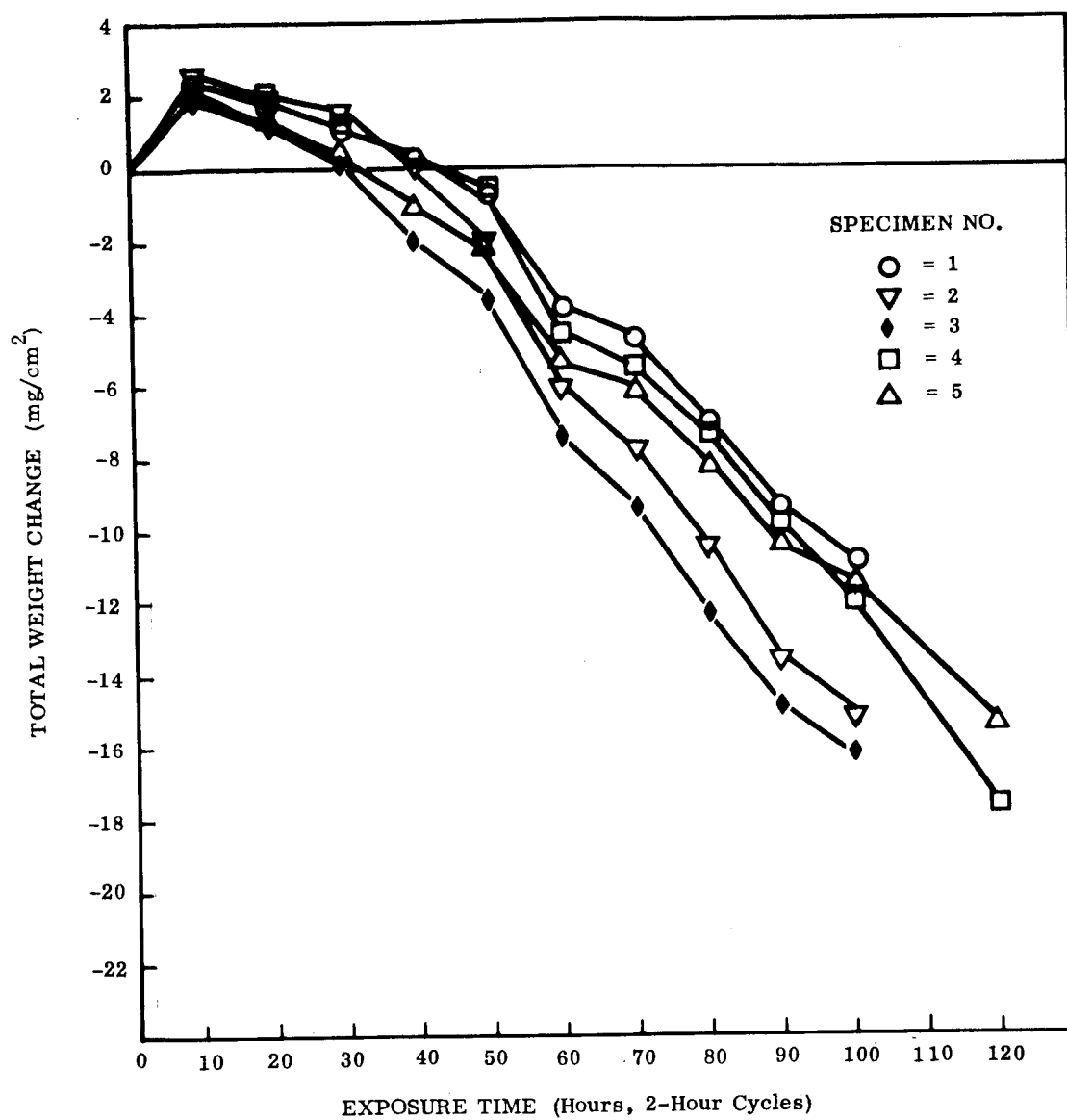


FIGURE 53. OXIDATION DATA FOR (Cr-5W)-Si; 2400 F

on the weight change coordinates for the three test temperatures, which tend to magnify the small variations ( $\pm 1 \text{ mg/cm}^2$ ) in weight change at the lower temperatures. Roughly parabolic oxidation rates (weight increase) were observed at 1500 F and initially at 2100 F, but increased amounts of spalling and the chromium loss by vaporization which occurred with longer times and higher temperatures make analysis of the thermogravimetric data unrealistic. The total weight changes however, are a very good indication of the coating stability.

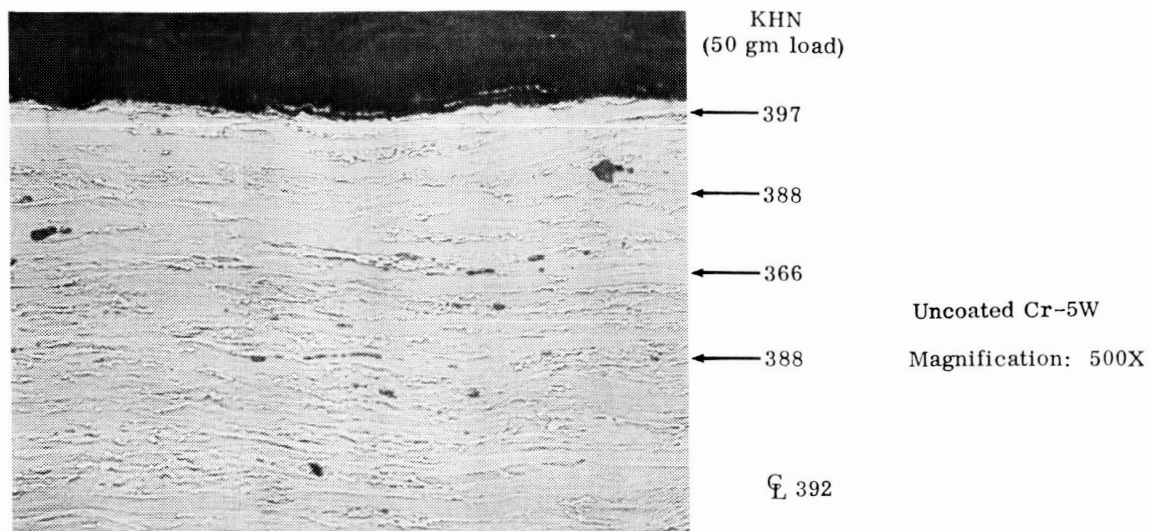
Compared to the refractory alloys of columbium and tantalum, the chromium alloy has extremely good oxidation resistance in the uncoated conditions; from visual examination and weight change data, it is difficult to determine at what point failure has occurred. In fact, catastrophic failure does not occur, rather a gradual deterioration by spalling takes place. An evaluation of the coating efficiency, therefore, must be made largely by metallography and quantitative gas analyses, with visual examination and weight change data serving to indicate the oxidation resistance and resistance to spalling of the coating.

Microstructures after testing at the three temperatures (1500, 2100, and 2400 F) are shown in Figures 54 through 58. Total weight changes and vacuum fusion analysis results after the maximum times tested are presented in Table XI.

Little change occurred in the as-received and as-coated microstructures after the 500-hour exposure at 1500 F (Fig. 47 and 54). The subsilicide ( $\text{CrSi}$ ) layer in the coated specimens increased in thickness by growing into the substrate so that the total silicide layer thickness increased to about twice that of the original  $\text{CrSi}_2$  and formation of  $\text{Cr}_5\text{Si}_3$  had just begun. Vacuum fusion analysis indicated some nitrogen contamination in the uncoated specimen (from 22 to 780 ppm  $\text{N}_2$ ) but the range of oxygen values were about the same before and after testing exposure.

The sample coated with silicide, however, showed a reduction in both oxygen (1000  $\rightarrow$  85 ppm) and nitrogen (22  $\rightarrow$  not detectable) content after 500 hours exposure. This is not unrealistic since on a thermodynamic basis, it should be possible for silicon (which forms a very stable oxide and nitride) to reduce the level of these interstitials in chromium to below the equilibrium solubility values (Appendix I).

At 2100 F, the uncoated alloy appeared to have good stability with oxide-spall occurring rather slowly and, after 500 hours, a positive weight increase ( $8.2$  to  $10.3 \text{ mg/cm}^2$ ) was recorded. However, rapid internal oxidation with heavy grain



Magnification: 500X



Magnification: 100X

FIGURE 54. UNCOATED Cr-5W AND (Cr-5W)-Si AFTER OXIDATION TESTING; 500 Hours at 1500 F

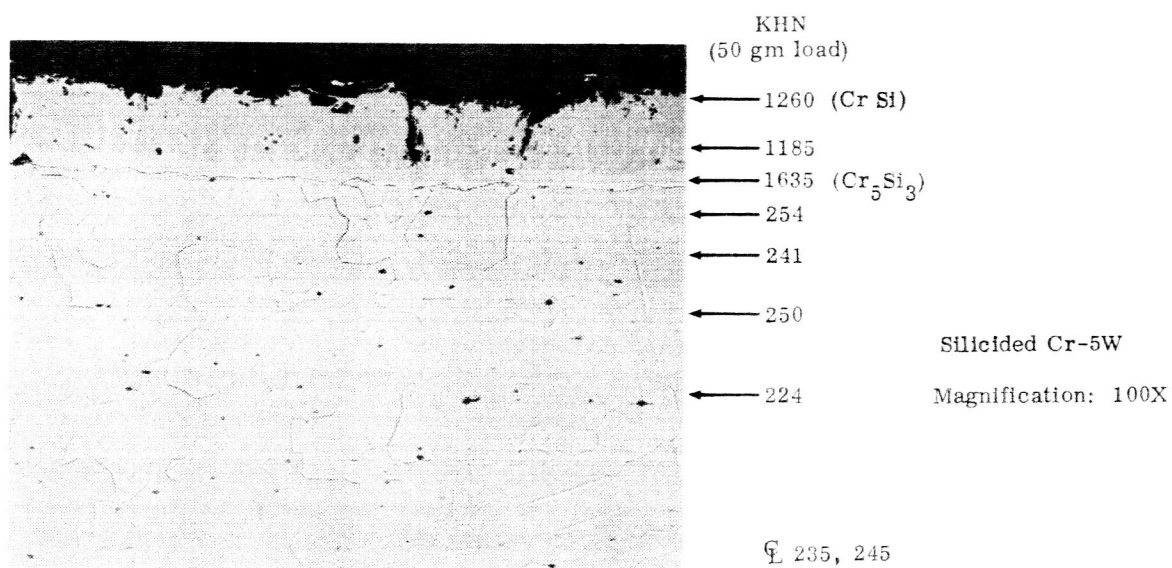
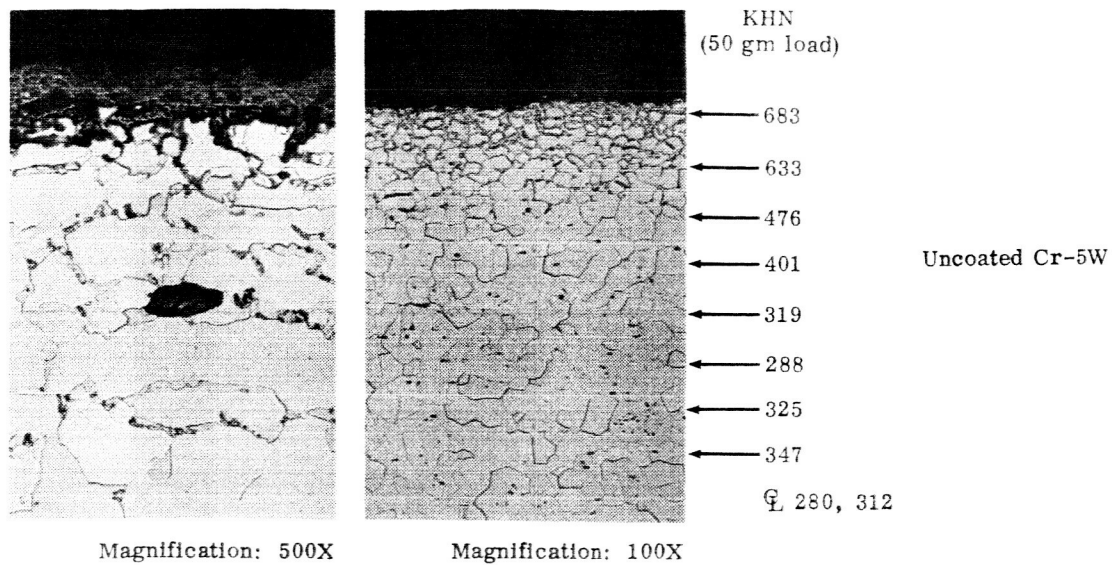


FIGURE 55. UNCOATED Cr-5W AND (Cr-5W)-Si AFTER OXIDATION TESTING; 114 Hours at 2100 F

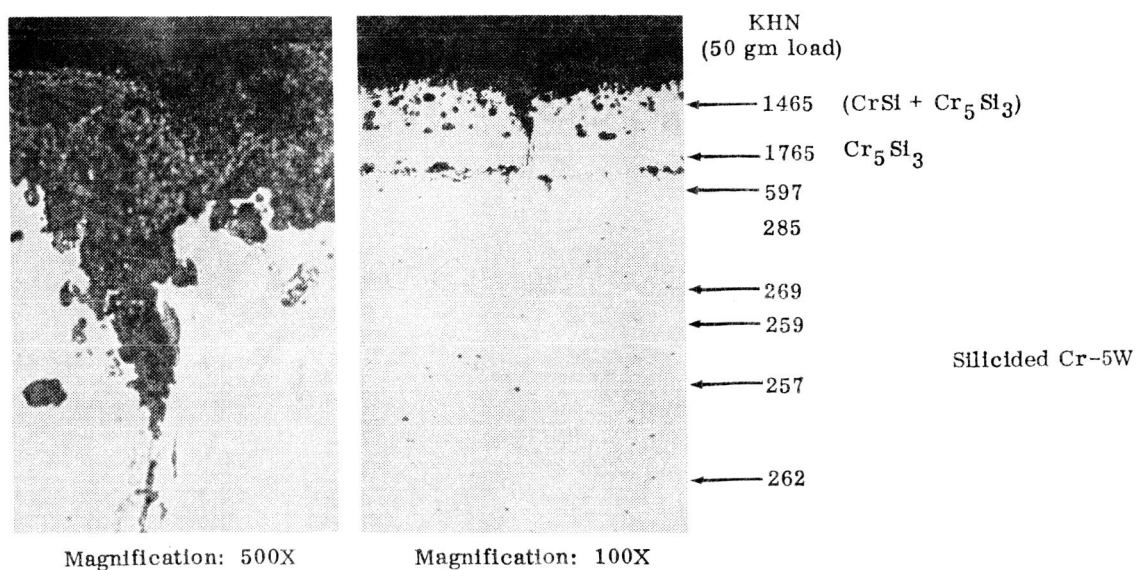
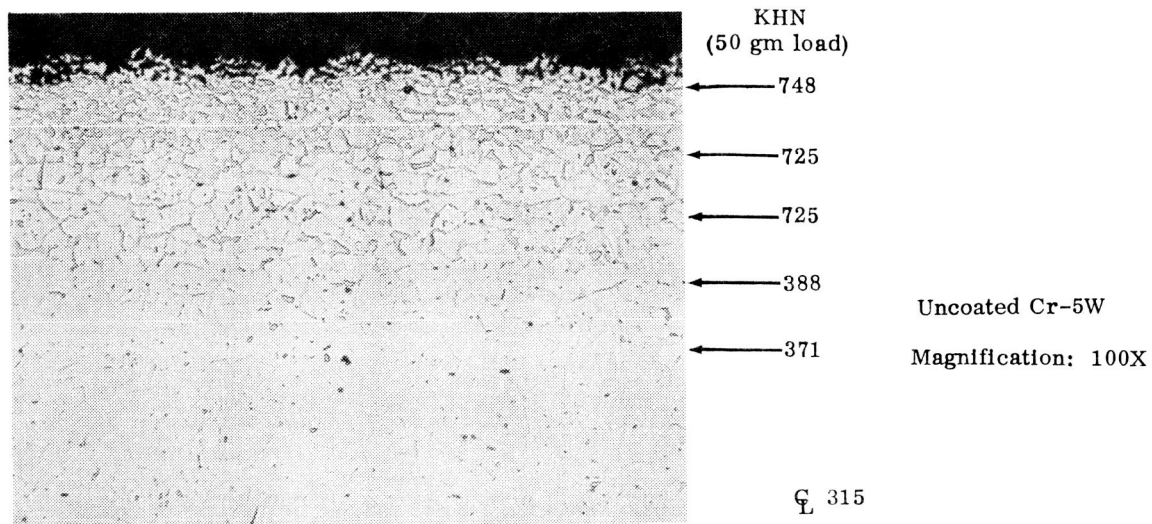


FIGURE 56. UNCOATED Cr-5W AND (Cr-5W)-Si AFTER OXIDATION TESTING; 500 Hours at 2100 F

boundary precipitation occurred as shown in Figures 55 and 56. No evidence of nitride needle precipitation was observed. Considerable volume expansion was required to accommodate this precipitate and specimens were thicker after 500 hours exposure than at the start of the test even though spalling of surface oxide occurred steadily. Oxygen and nitrogen values had increased to 0.4 and 0.67 weight percent, respectively. The silicide coating was rapidly converted to  $\text{CrSi}$  and  $\text{Cr}_5\text{Si}_3$ . After 114 hours no  $\text{CrSi}_2$  remained (Fig. 55); after 500 hours, the silicide was almost all converted to  $\text{Cr}_5\text{Si}_3$  (Fig. 56). The hardness data indicated that only slight diffusion of silicon into chromium occurred beyond the silicide/chromium alloy interface. This coating seemed to afford complete protection to the substrate since after 500 hours cyclic exposure, recorded oxygen and nitrogen values were 80 to 100 ppm and 67 to 70 ppm, respectively. Deterioration of the coating occurred by formation of  $\text{Cr}_2\text{O}_3$  and (presumably)  $\text{SiO}_2$ , which are virtually immisible and do not form a protective glass. Steady spalling of green, powdery,  $\text{Cr}_2\text{O}_3$  was observable during testing.

At 2400 F, the same reactions occurred, but took place more rapidly. Figure 57 shows that a 90-hour exposure of the uncoated specimens was sufficient to convert most of the 0.060-inch thick specimens to Cr-O-N compound, and weight losses were recorded from the beginning of the test (Fig. 52). Metallography and vacuum fusion analyses indicated that the compound phase was largely nitride; this would be the case if nitrogen diffusion rates are considerably higher than oxygen diffusion rates in chromium, and if a surface nitride is a good oxygen diffusion barrier. This would then explain the anomalously low oxygen value of 740 ppm recorded in this particular sample.

The silicide coating appeared (visually) to be in good condition after 50 hours at 2400 F, where weight losses of  $-0.6$  to  $-3.8 \text{ mg/cm}^2$  were recorded. After this time, an accelerated rate of spalling was noticed. The general microstructures after 100 hours exposure is shown in Figure 58. Because of extensive coating spalling, nitrogen was able to leak through the  $\text{Cr}_5\text{Si}_3$  to form nitride needles within the chromium alloy matrix. Vacuum fusion analyses after 120 hours exposure gave values of 490 ppm  $\text{O}_2$  and 120 ppm  $\text{N}_2$  (Table XI). Total weight losses after this time were  $-15$  to  $-18 \text{ mg/cm}^2$ , compared to  $-34$  to  $-38 \text{ mg/cm}^2$  after 90 hours exposure for the uncoated specimens and, in the former case, were due to spalling of the coating alone. However, this 0.002-inch thick (initially  $\text{CrSi}_2$ ) silicide coating was insufficient to prevent nitrogen contamination of the substrate for 100 hours exposure at 2400 F.





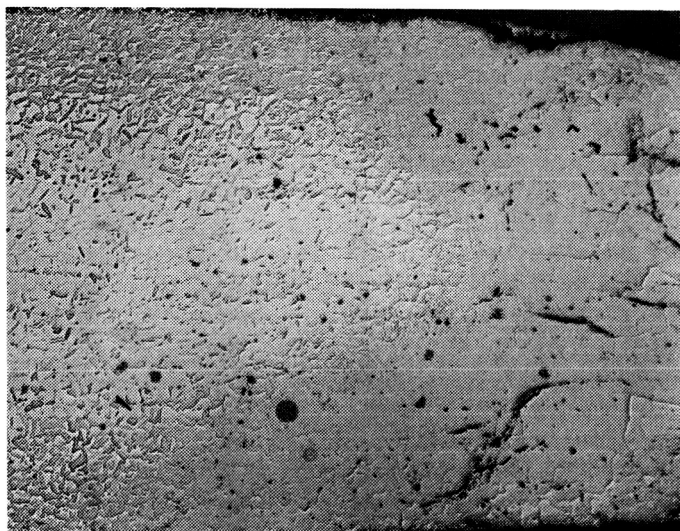
Magnification: 500X



Magnification: 100X

A

After Oxidation Testing  
50 Hours at 2400 F



B

After Oxidation Testing  
90 Hours at 2400 F

Magnification: 50X

FIGURE 57. UNCOATED Cr-5W ALLOY AFTER OXIDATION TESTING

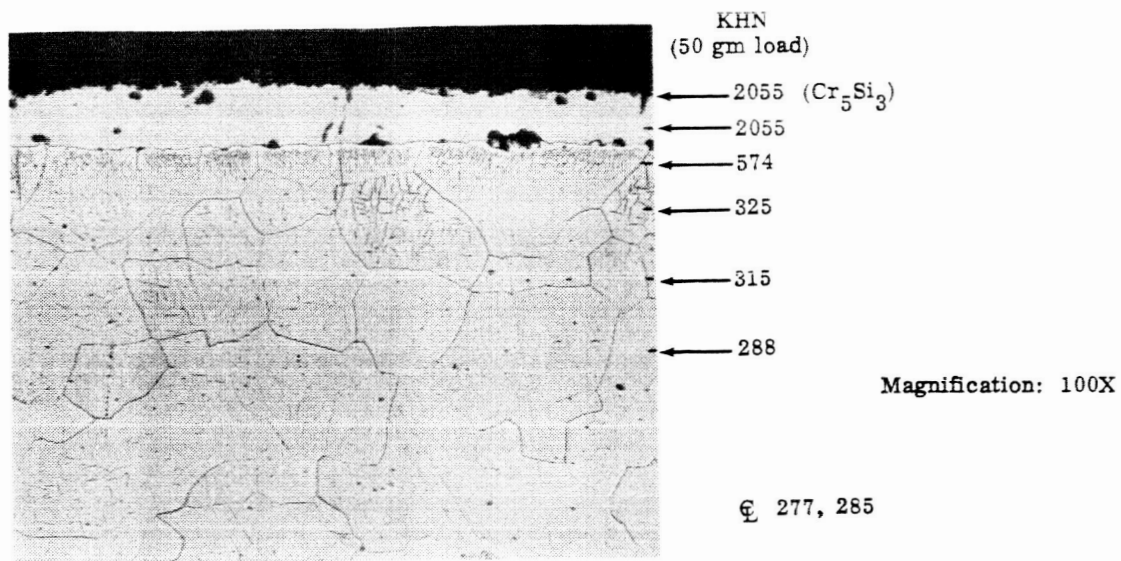


FIGURE 58. (Cr-5W)-Si AFTER OXIDATION TESTING; 100 Hours  
at 2400 F

TABLE XII

OXIDATION TEST DATA, 2400 F

Specimen No.	Coating Layer (mg/cm <sup>2</sup> )				Total Weight Change (mg/cm <sup>2</sup> )							
	V	Ti	Mo	Si	6 Hours	21 Hours	22 Hours	27 Hours	37 Hours	52 Hours	71 Hours	91 Hours
A (1)	10	25		22	0.86		1.31		-4.82			
(2)	10	25		22	1.54	1.96		-14.4				
B	10	15		24.7	1.50		3.03		-12.17*			
C (1)	8.2	20		18.8	0.98		1.92		-12.36	-18.47	-22.95	
(2)	8.2	20		18.8	0.77	1.16		0.61				
2000	4			41	-2.17		-2.09		-34.83	-48.41	-62.18+	
2010	8			26.7	-1.11		-4.09		-12.97*			
2110	11			22.3	-1.95		-3.73		- 6.17	-12.75	-23.29	
14	10	22	50	20	-5.62		-9.98		-52.35+			
27	10		50	21.5	-23.7		-72.11+					
* Removed for Metallographic Examination + Failed												

### 5.2.2 Oxidation Testing of V-Ti-Mo-Si Coatings

Because of the processing problems discussed in Section IV, it was not possible to produce coated specimens which satisfied all of the composition requirements for the original concept. Specimen sizes were reduced to 1/2 inch by 3/4 inch to utilize available vanadium retorts, but deterioration of these retorts and processing difficulties restricted the vanadium layer thickness to 0.00075 inch (instead of 0.002 inch). Since all coating compositions required vanadium as the sublayer, the number of test specimens was reduced, and only the 2400 F tests were conducted.

Nevertheless, the results obtained from these tests indicated certain undesirable features of this multilayer coating (the presence of unalloyed vanadium and/or molybdenum) which were not anticipated and which might still be a problem even if optimum deposition of the component metals were achieved.

Coating compositions and weight gain data after testing at 2400 F are shown in Table XII. Exposure times were accumulated by running 2-hour cycles, 15-hour cycles (overnight), and in two instances, 64-hour cycles to accumulate sufficient test time. Microstructures of the as-coated A and C specimens are shown in Figures 59 and 60. Vanadium appeared to be a diffusion barrier for silicon. Where the silicide penetrated through to the V-Ti/Cr interface, rapid bulk diffusion of silicon took place, and resulted in formation of CrSi (Fig. 59, 100X magnification); but where a vanadium-rich diffusion zone was still evident, grain boundary penetration of silicon occurred forming discrete silicide particles.

During the initial exposures at 2400 F, a green/brown glaze was formed on the samples (quite unlike the matte-green surface obtained with the unmodified CrSi<sub>2</sub> coating) and deep craze cracks were observed (Fig. 61 and 62). With continued exposure, the glaze slowly disappeared and the coating surface more closely resembled that of CrSi<sub>2</sub> or CrSi, indicating that volatile V<sub>2</sub>O<sub>5</sub> is an important constituent of the oxide glass. With the disappearance of this glass, spalling of the coating became quite severe as can be seen from the recorded weight losses (Table XII). The microstructures after 91 hours at 2400 F (Fig. 63 and 64) showed that better protection was afforded to the substrate than weight losses and surface appearance indicated. Gas analyses were not carried out on these samples, but the absence of nitride needles indicated the presence of less than 100 ppm nitrogen. However, the coating was very porous and definitely did not show promise of greater than 100 hours life at 2400 F because

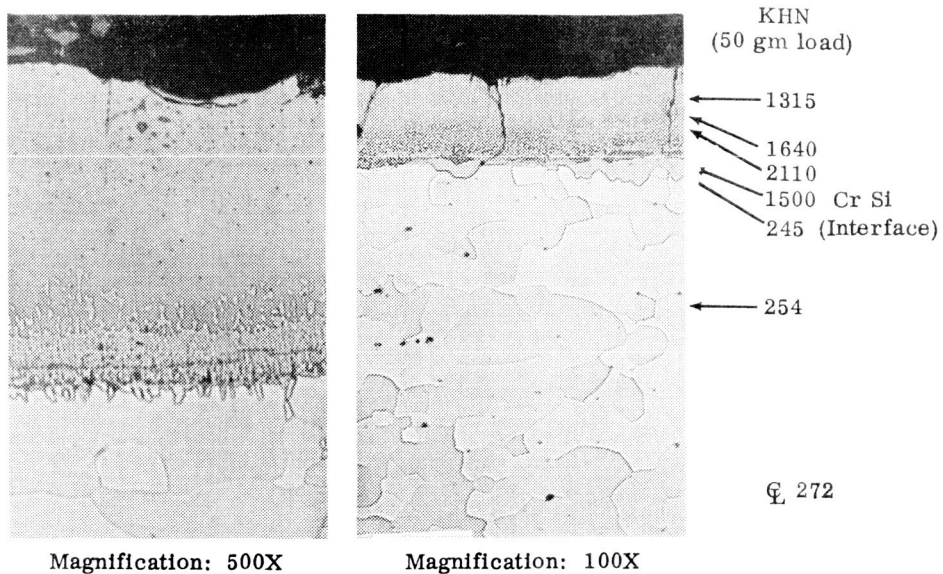


FIGURE 59. AS-COATED (Cr-5W)-V-Ti-Si; Specimen A

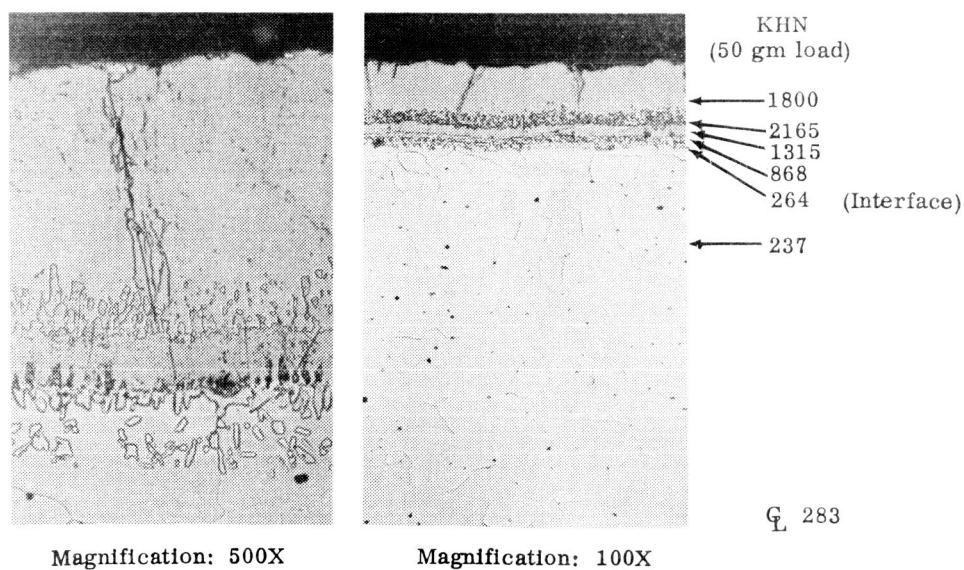
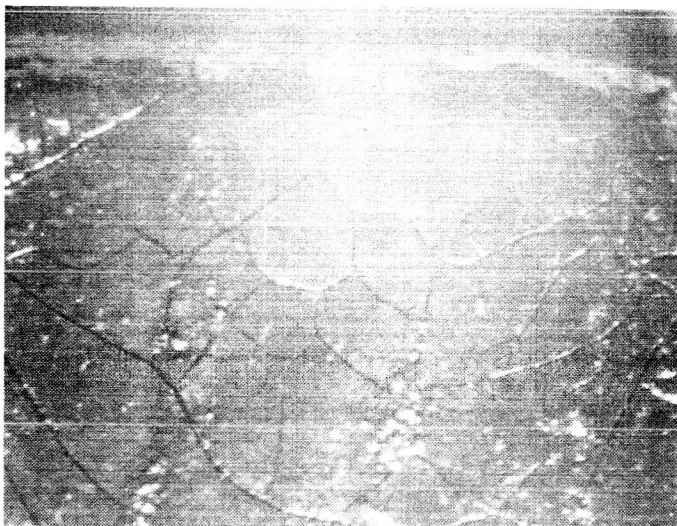


FIGURE 60. AS-COATED (Cr-5W)-V-Ti-Si; Specimen C



Magnification: ~10X

FIGURE 61.

COATED (Cr-5W)-V-Ti-Si  
AFTER OXIDATION TESTING;  
6 Hours (3, Two-Hour Cycles)  
at 2400 F, Specimen A



Magnification: ~10X

FIGURE 62.

COATED (Cr-5W)-V-Ti-Si  
AFTER OXIDATION TESTING;  
6 Hours (3, Two-Hour Cycles)  
at 2400 F, Specimen C

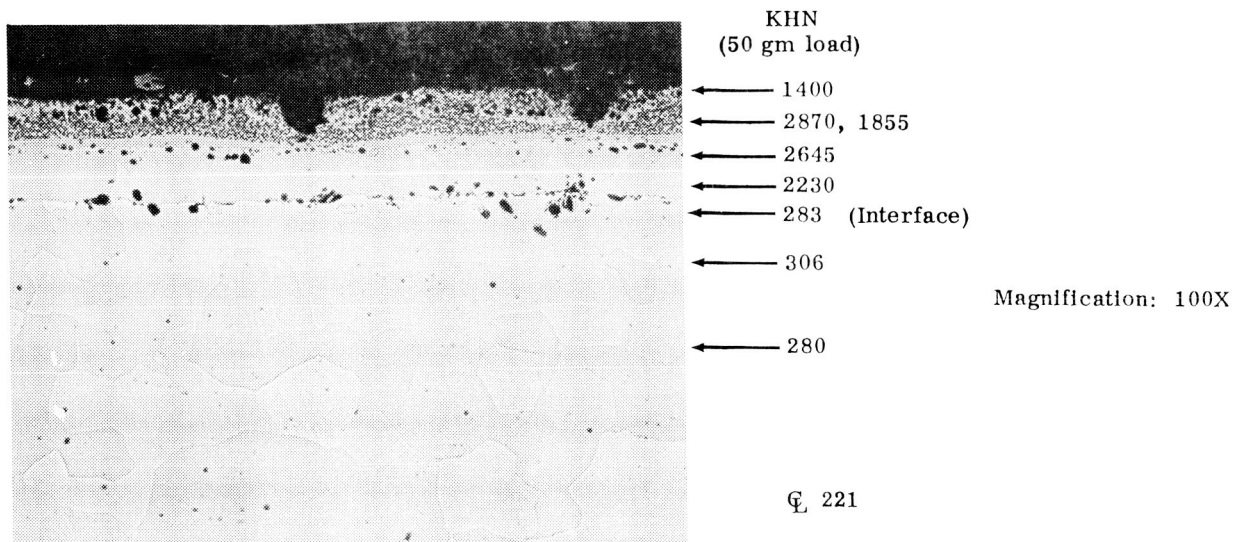


FIGURE 63. COATED (Cr-5W)-V-Ti-Si AFTER OXIDATION TESTING;  
91 Hours at 2400 F, Specimen A

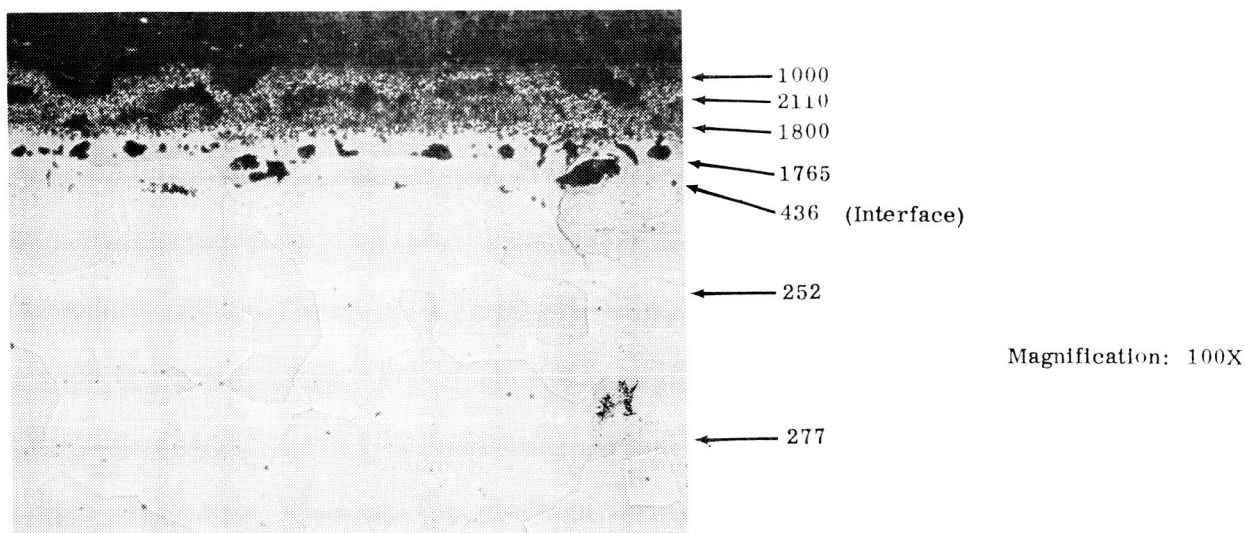


FIGURE 64. COATED (Cr-5W)-V-Ti-Si AFTER OXIDATION TESTING;  
91 Hours at 2400 F, Specimen C



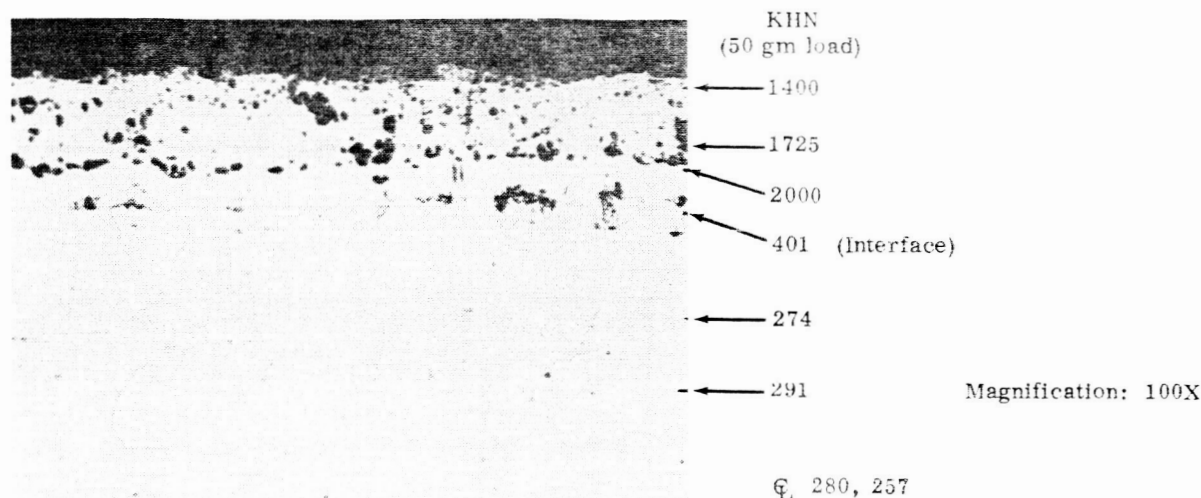


FIGURE 65. COATED (Cr-5W)-V-Ti-Si AFTER OXIDATION TESTING;  
52 Hours at 2400 F, Specimen 2010

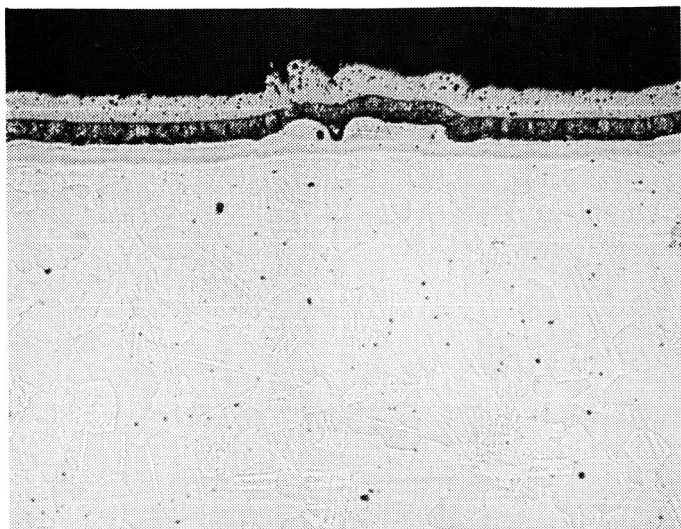
of the accelerated spalling rate. It would appear that loss of vanadium and/or titanium as volatile oxides was responsible for the porosity that developed, which in turn, caused severe spalling because of poor mechanical bond.

Coating compositions 2000, 2010, and 2110 (Table XII), the (Cr-5W)-V-Si series, behaved in a very similar manner but the oxide glass was lost after less exposure time than noted for the V-Ti-Si coating resulting in more rapid spalling. Considerable porosity developed in the coating but no substrate contamination was visible in Specimen 2010 after 52 hours exposure (Fig. 65).

The coatings containing molybdenum (V-Mo-Si and V-Ti-Mo-Si) resulted in such severe corrosion of the substrate during the 2400 F exposure that it was not possible to prepare samples for metallographic study. The as-coated samples are shown in Figures 66 and 67. After three 2-hour cycles, very extensive break-away of the coatings occurred, exposing metallic vanadium and molybdenum to the atmosphere, which in turn resulted in formation of highly corrosive  $V_2O_5$  and  $MoO_3$ .

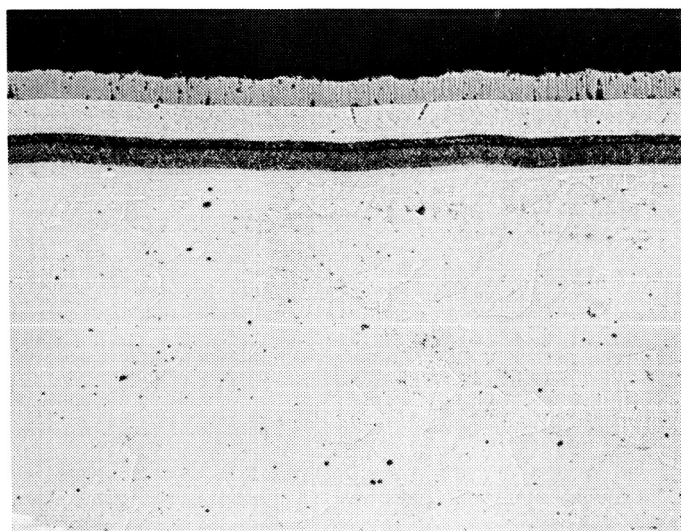
The reason for the severe spall and break-away which occurred in the case of the V-Ti-Mo-Si coating is quite evident from Figure 68. An almost continuous crack was formed in the titanium-rich layer (even before test exposures) and the high magnification photograph in Figure 68 indicates that small cracks were first formed in the  $\alpha$  platelets or possibly in a continuous  $\alpha$  solid solution zone. A  $\beta$  stabilizer exists





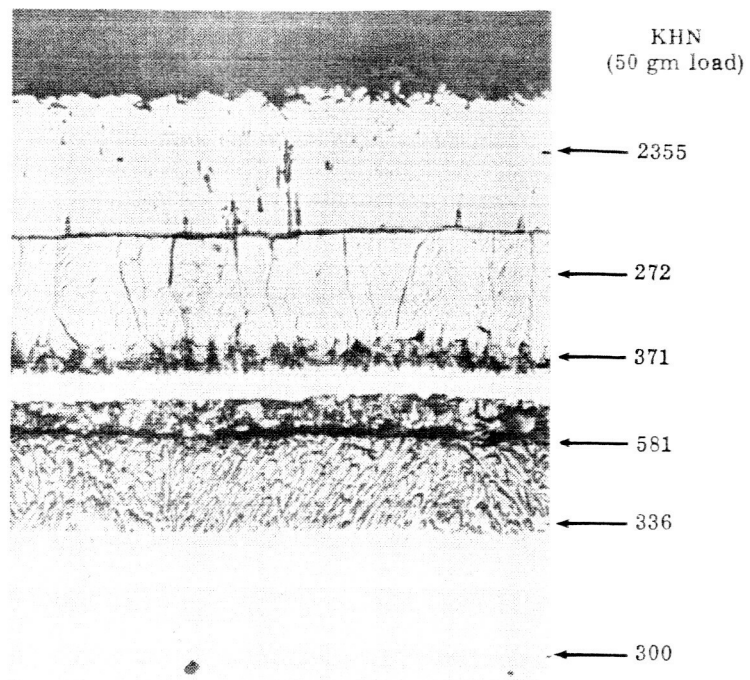
Magnification: 100X

FIGURE 66.  
AS-COATED (Cr-5W)-V-Mo-Si

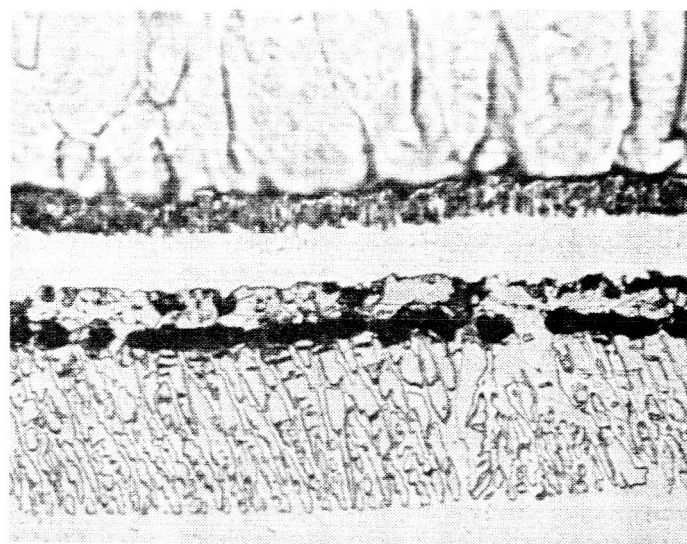


Magnification: 100X

FIGURE 67.  
AS-COATED (Cr-5W)-V-Ti-Mo-Si



Magnification: 500X



Magnification: 1000X

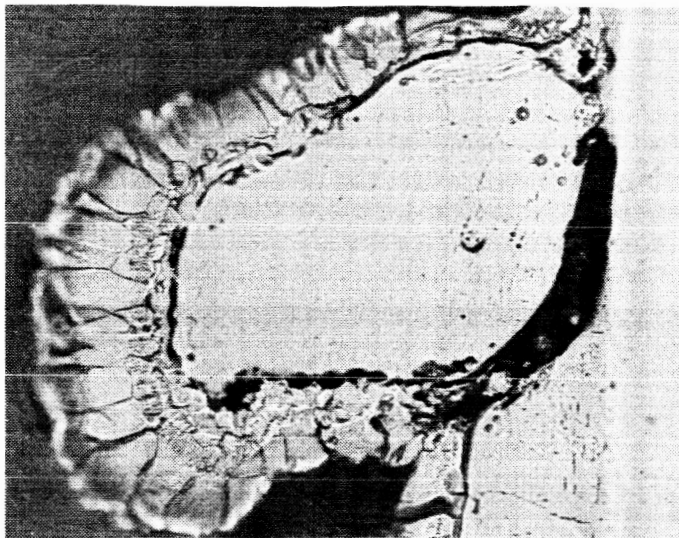
FIGURE 68. AS-COATED Vi-Ti-Mo-Si COATING

on either side of the titanium layer (Mo and V) but, as shown in the interstitial sink studies, the titanium layer would rapidly pull oxygen and nitrogen from these two metals which would have the opposing effect of stabilizing the  $\alpha$  phase. It is likely, therefore, that cracking occurred in an embrittled, oxygen-rich zone, an observation which is supported by the microhardness data, during the thermal cycling involved in processing. In subsequent oxidation testing, severe stresses were induced in the coating due to considerable differences in coefficients of expansion between the silicide and various metallic layers. This resulted in cracks being extended and provided free access of air to vanadium and molybdenum-rich alloy sublayers. Formation of highly corrosive  $V_2O_5$  and  $MoO_3$  occurred, resulting in a significantly accelerated corrosion rate of the substrate compared to the uncoated material. An additional problem may be posed by the nonuniform vanadium deposits as shown in Figure 69. The sintered vanadium granule in Figure 69 would make an ideal area for activator entrapment and  $V_2O_5/MoO_3$  concentration which would lead to accelerated corrosion attack. Any such microdefects present in a test specimen would clearly encourage rapid deterioration in the coating sublayers once oxygen was able to penetrate through the outer barrier.

Weight change data in Table XII show that the V-Mo-Si coating was even more unstable, and could not be explained by the presence of interface cracking. After the first 2-hour cycle, the light-gray  $MoSi_2$  appeared to have excellent stability, but only an additional two cycles were required to cause the break-away of large areas of coating. Subsequent formation of  $V_2O_3$  caused greatly accelerated corrosion of the substrate.

It is not immediately apparent why  $MoSi_2$  over molybdenum/vanadium should have such poor thermal stability compared to  $CrSi_2$  since, in the former case, differences in coefficients of thermal expansion between coating and substrate layers are relatively small.

It has been reported (Ref. 19) however, that silicides obey a similar homologous temperature dependency for plasticity as metals do for diffusion controlled creep. Thus, a temperature of  $0.6 T_m$  for  $CrSi_2$  and  $MoSi_2$  is 1990 and 2550 F, respectively. On this basis, it might be assumed that at a test temperature of 2400 F,  $CrSi_2$  is well within the temperature region for plastic flow, while  $MoSi_2$  is still behaving elastically. Once a large crack propagated down to the molybdenum/vanadium layer, rapid oxidation of the substrate would take place with formation of liquid phase corrosive oxides.



Magnification: 500X

Area showing sintered granule of vanadium forming a potential corrosion pocket.

FIGURE 69. VANADIUM-MOLYBDENUM COATING ON Cr-5W ALLOY

# 6

## CONCLUSIONS

Although processing difficulties in the application of rhenium and vanadium to Cr-5W alloy prevented the uniform application of the metallic nitrogen barrier coating, Re-(Ti, Cr, V)-Si, and the nitrogen sink coating, V-(Ti, Mo)-Si, sufficient data were generated to show a major weakness in both systems. In both concepts, unalloyed Re, V, or Mo exists beneath the silicide primary oxygen barrier. When defects are generated in the silicide, the low melting oxides formed from these metals ( $V_2O_5$ ,  $MoO_3$ , and  $Re_2O_7$ ) can produce accelerated or catastrophic oxidation of the substrate. By siliciding completely through the modified layers as shown in the V-Si and V-Ti-Si systems, the catastrophic oxidation of the substrate could be eliminated; however, the oxidation life of these coatings appears to be limited to approximately 100 hours at 2400 F due to the development of porosity and subsequent spalling.

The simple silicide coating was also studied. Oxidation tests on specimens coated with  $14 \text{ mg/cm}^2$  of silicon showed that complete protection of the substrate could be effected for at least 500 hours at 1500 and 2100 F. Nitrogen and oxygen could be maintained below 100 ppm for the 500-hour test. At 1500 F, the silicide coating appeared to be an effective getter for oxygen and nitrogen. This coating lowered the oxygen content from 1500 ppm, as-received, to 100 ppm and lowered the nitrogen content from 22 ppm to not detectable. Life of the silicide coating at 2400 F was less than 120 hours due to continuous spalling; however, the spall rate was less than for the nitrogen sink coatings. The effectiveness of the silicide coating can perhaps best be illustrated by a comparison of nitrogen contents between the silicided and uncoated Cr-5W alloy after 500 hours of exposure at 2100 F. These values are 67 ppm and 6700 ppm respectively. The depth of silicon diffusion after testing was also minimal at this temperature.

Experimental data generated in the program showed that the basic premises on which the concepts were selected are valid, and that:

- Vanadium greater than 30 percent will destabilize the primary Ti-Cr<sub>2</sub> Laves phase.

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- Titanium and/or vanadium are effective sinks for the oxygen and nitrogen in chromium alloys.
- Rhenium and chromium do not develop a brittle  $\sigma$  phase in a detectable thickness when diffusion bonded together and heated for 30 hours at 2400 F.

In process development, the major emphasis was on the deposition of vanadium on the Cr-5W alloy. Four processes were used to deposit this element, high- and low-pressure packs and electrolytic and nonelectrolytic fused salts. Low-pressure pack deposition produced the most uniform deposit and was the technique adopted for coating the test specimens.

Techniques for deposition of rhenium on chromium were not sufficiently far advanced to provide satisfactory coatings. Consequently, the rhenium-nitrogen barrier concept was not evaluated.

Deposition of titanium over chromium or vanadium by nonelectrolytic fused salt technique provided outstanding coverage at rapid rates (0.0005 inch per hour).

Molybdenum was readily deposited over titanium or vanadium by the chemical vapor deposition technique.

The high-pressure pack siliciding process was used effectively to silicide the various samples.

# 7

## RECOMMENDATIONS

Further development of the two concepts proposed in this program, i.e., Re-(Ti, Cr, V)-Si and V-(Ti, Mo)-Si is not recommended. The presence of unsilicided rhenium, vanadium, or molybdenum can result in the formation of low melting point oxides that can have an adverse effect on the ability of the chromium alloy to protect itself when the silicide coating is damaged.

The simple silicide coating and minor modifications of it to increase the vitrification of the silica glass and lower its softening temperature appear to offer greater potential for future research. If layered modifiers are used, siliciding completely through the modifiers is recommended to minimize catastrophic oxidation failures. The effectiveness of silicon as a barrier and getter for oxygen and nitrogen precludes any necessity of providing secondary elements for this purpose.

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## APPENDIX I

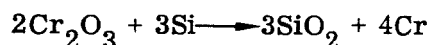
### PARTITION OF OXYGEN BETWEEN SILICON AND CHROMIUM

## APPENDIX I

### PARTITION OF OXYGEN BETWEEN SILICON AND CHROMIUM

To evaluate the equilibrium partition that would exist between oxygen and the two elements, silicon and chromium, the following may be calculated:

Assume the simple reaction:



$$2\text{Cr}_2\text{O}_3 = 4\text{Cr} + 3\text{O}_2; \Delta F^\circ_{1500 \text{ F}} = +406,500 \text{ cal}$$

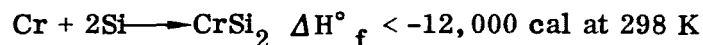
$$3\text{Si} + 3\text{O}_2 = 3\text{SiO}_2; \Delta F^\circ_{1500 \text{ F}} = -468,900 \text{ cal}$$

---


$$2\text{Cr}_2\text{O}_3 + 3\text{Si} \longrightarrow 3\text{SiO}_2 + 4\text{Cr}; \Delta F^\circ_{1500 \text{ F}} = -62,400 \text{ cal}$$

This value indicates that chromic oxide will be essentially reduced by pure silicon. The occurrence of silicon as the silicide will not change the thermodynamics appreciably.

The driving force of the reaction would be reduced by the bonding free energy of the Cr-Si compounds, but this bonding energy is small enough to be insignificant. Published data gives:



Review of data for silicides show that the heat of formation is usually close to the free energy of formation. It is a reasonable assumption that this holds for chromium silicides, in which case the free energy change for reaction between chromium oxide and chromium silicide is approximately -47,000 cal.

This effective  $\Delta F^\circ$  value is sufficiently negative for the oxides of chromium to be strongly reduced by the silicides of chromium.

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In addition, oxygen in solution in chromium will be reduced by silicon or chromium silicides. The data in Reference 2 show that the magnitude of oxygen remaining in solution at 1100 K could be of the order of 1 ppm after equilibration if there is low solubility of oxygen in silicon or silicides.

The actual experimental conditions are more complex because of the presence of tungsten, yttrium, nitrogen, and other elements. However, the experimental results showed that in 500 hours at 1500 F the oxygen content in the chromium coated with silicon and tested in air had been reduced from the order of 1000 ppm to below 100 ppm (Table XI of Section 5.2).

APPENDIX II  
MATERIALS

## APPENDIX II

### MATERIALS

The starting materials utilized to coat the chromium specimens were vanadium, titanium, silicon, molybdenum, rhenium, LiF, NaF,  $K_2TiF_6$ , and  $K_2VF_5$  or  $K_3VF_6$ .

Initial studies were performed on pure chromium specimens which were prepared by arc-melting iodide chromium in an inert (argon) atmosphere. These specimens were used for coating work prior to receipt of the program Cr-5W alloy sheet. The iodide chromium was obtained from the Chromalloy Corporation. Chemical analysis fixed the impurity level to be:

<u>Element</u>	<u>Analysis (%)</u>
Carbon	0.020
Nitrogen	0.016
Oxygen	0.06

The program chromium Cr-5W alloy sheet was obtained by Lewis Research Center from General Electric Co., Refractory Metals Plant.

Ingot analysis supplied by General Electric showed the elemental composition:

<u>Element</u>	<u>Analysis</u>
Tungsten	$4.82\% \pm 0.06\%$
Yttrium	0.064%
Sulfur	$40 \pm 10$ ppm
Phosphorus	<30 ppm

The ductile brittle transition temperature of the sheet product was reported to be  $\approx 1100$  F. The analysis of the sheet fixed the interstitial levels at:

<u>Element</u>	<u>Analysis (%)</u>
Oxygen	0.1
Nitrogen	0.01

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Vanadium granules were obtained from Union Carbide Corporation. The granules were -8 + 20 mesh with an oxygen content of <0.1 percent and an iron content of <0.12 percent.

The titanium and  $K_2TiF_6$  used for fused salt deposition were commercially pure.

The NaF and LiF were analytical reagent grade.

The  $K_2VF_5$  or  $K_3VF_6$  was synthesized at Solar from vanadium granules reacted with analytical reagent grade chemicals.

The silicon from Union Carbide Corporation was 99.06 percent pure, and analysis fixed impurities at:

<u>Element</u>	<u>Analysis (%)</u>
Calcium	0.03
Iron	0.34
Oxygen	0.02

The molybdenum was deposited by San Fernando Laboratories by reacting chlorine with molybdenum shavings to produce the reaction gas. Rhenium was also deposited by San Fernando Laboratories.

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